

USSR/Cultivated Plants. Fodder Plants.

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Abs Jour : Ref Zhur-Biol., No 15, 1953, 68203

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Cultivation.

Title : A Green Conveyor of Perennial Grasses.

Orig Oub : Inform. byul. Nauk.-dosl. in-t zemlerobstva  
i tvarinnitstva zakhidn, rayoni v URSR, 1957,  
No 2, 38-41.

Abstract : On the basis of investigations made on the  
the experimental fields of the Lvov Scientific  
Research Institute of Field Cultivation,  
a green conveyor scheme is recommended for  
the western rayons of the Ukraine. Over the  
course of 100-120 days, green fodder springs  
up from the perennial grasses sown in the

Card : 1/2



Stored VI with  $\text{SnCl}_4$  gives Hg (only after boiling many hrs.), XII and an org. Sn compd. The reactions of stored VI resemble closely those of the simple alkyl I as to slowness and products. Recryst. of stored VI does not give a product with the properties of freshly prepd. VI. The reactivity of the Sn compd. used depends directly upon its only.  $\text{SnF}_4$  and  $\text{SnSO}_4$  react very slowly, and  $\text{SnI}_4$  not at all. Therefore, if fluorides or sulfates of org. Sn are desired, an indirect method by way of the corresponding chloride should be used. The nature of the reaction between compds. of type II and  $\text{SnX}_4$  depends on the org. radical, the solvent, and the X linked with Hg and Sn. X and XII with  $\text{SnCl}_4$  react thus:  $2\text{RHgCl} + 2\text{SnCl}_4 \rightarrow \text{R}_2\text{SnCl}_2 + 2\text{Hg} + \text{SnCl}_4$  (D) in either EtOH or  $\text{Me}_2\text{CO}$ . There is no reduction to RH, although the reaction  $\text{RHgX} + \text{SnX}_4 \rightarrow \text{R}_2\text{SnX}_2 + \text{Hg}$  (E) occurs to a very slight extent. XV with  $\text{SnCl}_4$  follows (D) in  $\text{Me}_2\text{CO}$ . In EtOH the reaction is  $\text{RHgCl} + \text{SnCl}_4 + \text{EtOH} \rightarrow \text{RH} + \text{Hg} + \text{EtOSnCl}_3$  (F). With  $\text{SnBr}_4$  the principal reaction is  $2\text{RHgBr} + \text{SnBr}_4 \rightarrow \text{R}_2\text{SnBr}_2 + 2\text{HgBr}$  (G). With ppt. obtained in either wholly  $\text{HgBr}$ , e.g., with XI, or  $\text{HgBr}$  admixed with a smaller quantity of Hg. The Hg probably arises by reaction (E). (E) may also explain the formation of  $\text{p-tolylC}_6\text{H}_4\text{SnBr}_3$  (with *p*-tolylstannonic acid), but not that of phenylstannonic acid. XIV gives  $\text{HgBr}$  and also  $\text{C}_6\text{H}_5$ . XVII with  $\text{SnCl}_4$  reacts slowly with 80% elimination of free Hg. A very small quantity of org. Sn compd. is formed. XVI did not react during 15 hrs. boiling. The aromatic Hg compds. used were prepd. through the diazonium salts according to the method of Nesmeyanov (cf. C. A. 23, 5172). The importance of using absolutely anhyd. materials is emphasized and K. and N. attribute the failure of earlier workers to obtain satisfactory yields of org. Sn compds. by analogous methods to the presence of water. The generalizations made are: With compds. of type I the usual reaction is (A), but with slowly reacting substs. (A) is accompanied by other reactions such as (C) resulting in a mixt. of org. Sn compds. Aryl compds. of type I all react rapidly and according to (A) when the solvent is  $\text{Me}_2\text{CO}$ . In EtOH the reaction varies with different compds. When R is an unsubstituted ring or  $\text{PhCH}_2$ , the reaction is (A); if R contains side chains or is  $\text{C}_6\text{H}_5$ , RII is formed by reaction (B). Aromatic Hg chlorides react according to (D) even in EtOH, whereas the corresponding I follows (B). Aromatic Hg bromides react in 2 ways simultaneously, (D) and (G).



11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100 101 102 103 104 105 106 107 108 109 110 111 112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180 181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198 199 200 201 202 203 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 278 279 280 281 282 283 284 285 286 287 288 289 290 291 292 293 294 295 296 297 298 299 300 301 302 303 304 305 306 307 308 309 310 311 312 313 314 315 316 317 318 319 320 321 322 323 324 325 326 327 328 329 330 331 332 333 334 335 336 337 338 339 340 341 342 343 344 345 346 347 348 349 350 351 352 353 354 355 356 357 358 359 360 361 362 363 364 365 366 367 368 369 370 371 372 373 374 375 376 377 378 379 380 381 382 383 384 385 386 387 388 389 390 391 392 393 394 395 396 397 398 399 400 401 402 403 404 405 406 407 408 409 410 411 412 413 414 415 416 417 418 419 420 421 422 423 424 425 426 427 428 429 430 431 432 433 434 435 436 437 438 439 440 441 442 443 444 445 446 447 448 449 450 451 452 453 454 455 456 457 458 459 460 461 462 463 464 465 466 467 468 469 470 471 472 473 474 475 476 477 478 479 480 481 482 483 484 485 486 487 488 489 490 491 492 493 494 495 496 497 498 499 500 501 502 503 504 505 506 507 508 509 510 511 512 513 514 515 516 517 518 519 520 521 522 523 524 525 526 527 528 529 530 531 532 533 534 535 536 537 538 539 540 541 542 543 544 545 546 547 548 549 550 551 552 553 554 555 556 557 558 559 560 561 562 563 564 565 566 567 568 569 570 571 572 573 574 575 576 577 578 579 580 581 582 583 584 585 586 587 588 589 590 591 592 593 594 595 596 597 598 599 600 601 602 603 604 605 606 607 608 609 610 611 612 613 614 615 616 617 618 619 620 621 622 623 624 625 626 627 628 629 630 631 632 633 634 635 636 637 638 639 640 641 642 643 644 645 646 647 648 649 650 651 652 653 654 655 656 657 658 659 660 661 662 663 664 665 666 667 668 669 670 671 672 673 674 675 676 677 678 679 680 681 682 683 684 685 686 687 688 689 690 691 692 693 694 695 696 697 698 699 700 701 702 703 704 705 706 707 708 709 710 711 712 713 714 715 716 717 718 719 720 721 722 723 724 725 726 727 728 729 730 731 732 733 734 735 736 737 738 739 740 741 742 743 744 745 746 747 748 749 750 751 752 753 754 755 756 757 758 759 760 761 762 763 764 765 766 767 768 769 770 771 772 773 774 775 776 777 778 779 780 781 782 783 784 785 786 787 788 789 790 791 792 793 794 795 796 797 798 799 800 801 802 803 804 805 806 807 808 809 810 811 812 813 814 815 816 817 818 819 820 821 822 823 824 825 826 827 828 829 830 831 832 833 834 835 836 837 838 839 840 841 842 843 844 845 846 847 848 849 850 851 852 853 854 855 856 857 858 859 860 861 862 863 864 865 866 867 868 869 870 871 872 873 874 875 876 877 878 879 880 881 882 883 884 885 886 887 888 889 890 891 892 893 894 895 896 897 898 899 900 901 902 903 904 905 906 907 908 909 910 911 912 913 914 915 916 917 918 919 920 921 922 923 924 925 926 927 928 929 930 931 932 933 934 935 936 937 938 939 940 941 942 943 944 945 946 947 948 949 950 951 952 953 954 955 956 957 958 959 960 961 962 963 964 965 966 967 968 969 970 971 972 973 974 975 976 977 978 979 980 981 982 983 984 985 986 987 988 989 990 991 992 993 994 995 996 997 998 999 1000 1001 1002 1003 1004 1005 1006 1007 1008 1009 1010 1011 1012 1013 1014 1015 1016 1017 1018 1019 1020 1021 1022 1023 1024 1025 1026 1027 1028 1029 1030 1031 1032 1033 1034 1035 1036 1037 1038 1039 1040 1041 1042 1043 1044

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| 1ST AND 2ND ORDERS                                                                         |  |  |  |  |  |  |  |  |  | PROCESSING AND PREPARATION NOTES                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |  |  |  |  |  |  |  |  |  |
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| 1ST AND 2ND ORDERS                                                                         |  |  |  |  |  |  |  |  |  | PROCESSING AND PREPARATION NOTES                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |  |  |  |  |  |  |  |  |  |
| <p>  </p> |  |  |  |  |  |  |  |  |  | <p> <b>Properties of halomercaptobenzoic acids. A. N. NUSSEYANOV AND L. G. MAKAROVA.</b><br/> <i>J. Gen. Chem. (U. S. S. R.)</i> 3, 1162-3(1931); cf. <i>C. A.</i> 26, 4028. --The m. ps. of <i>halo-</i><br/> <i>mercaptobenzoic acids</i>, together with those found by König and Scharrbeck (<i>C. A.</i> 25,<br/>           927) and shown here in parentheses are: <i>o</i>-Cl 253° (251°), <i>o</i>-Br 249° (<i>o</i>-I has no definite<br/>           m. p.), <i>m</i>-Cl 264° (256°), <i>m</i>-Br 230°, <i>m</i>-I 181-5°, <i>p</i>-Cl 273° (272°) (<i>p</i>-Br and <i>p</i>-I, do<br/>           not melt).<br/>           CHAR. BLANC         </p> |  |  |  |  |  |  |  |  |  |
| <p>           480-564 METALLURGICAL LITERATURE CLASSIFICATION         </p>                 |  |  |  |  |  |  |  |  |  | <p>           627         </p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |  |  |  |  |  |  |  |  |  |
| <p>           1ST AND 2ND ORDERS         </p>                                              |  |  |  |  |  |  |  |  |  | <p>           PROCESSING AND PREPARATION NOTES         </p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |  |  |  |  |  |  |  |  |  |

**CIA-RDP86-00513R001136620C**



Organic compounds of mercury. A. M. Monaghan.  
*Uspoln. Khim. (U. S. S. R.)* 3, 4-20 (1954). — Aliphatic,  
 aromatic, Hg rings,  $\text{C}-\text{Hg}-\text{C}$ ,  $\text{C}-\text{Hg}-\text{C}-\text{C}$ ,  $\text{C}-\text{Hg}-\text{C}-\text{C}-\text{C}$ ,  
 $\text{Hg}-\text{X}$ ,  $\text{C}-\text{Hg}-\text{C}$ ,  $\text{C}-\text{Hg}-\text{C}-\text{C}$ , and other  
 types of bonds are considered. Syntheses of and use in  
 syntheses of other compounds are given for many types.  
 Unpublished work of Monaghan and co-workers is de-  
 scribed. 2-Aminopyridine on mercurization gives a 2-  
 substituted. Arylthiomers chloride- $\text{HgCl}_2$  double  
 substituted deriv. Arylthiomers chloride- $\text{HgCl}_2$  double  
 salts with organic Cu and Ag.  $\text{NH}_4$  give the corresponding  
 mercury diaryl compd. while with Ag powder alone the  
 mercury chloride is obtained. Hg derivs. of  
 arylthiomers chloride may be used to prep.  
 substituted benzoic acids and phenols. The yields are  
 satisfactory. benzoic acids and phenols. The yields are  
 good, and any desired isomer, including the meta, may  
 be prep. in pure form.  $\text{H}_2\text{NCO}_2\text{Et}$  with  $\text{HgCl}_2$  gives  
 the corresponding Cl ester and  $\text{Hg}(\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{COO})_2$ .  
 Displacement of  $\text{MeNH}_2$  by  $\text{HgCl}_2$  by action of  $\text{AmONO}$  in  
 the presence of  $\text{HgCl}_2$  with or without Cu gives small  
 amounts of  $\text{C}_6\text{H}_5\text{HgCl}$ . Arylthiomers chloride or  
 various dihalides, diarylmethanes chloride or  
 triarylmethanes with  $\text{HgO}$  in alk. soln. give diaryl-  
 mercury derivs. Pb and Sn compds. react analogously.

$\text{SnPh}_4$  on boiling in alc. with  $\text{HgCl}_2$  gives  $\text{PhHgCl}$ .  $\text{PhPh}_3$   
 reacts only slowly on boiling, and in alk. soln. yields  
 $\text{PhHgOH}$ . Doubtly but unsymmetrically substituted Hg  
 compds. of the type  $\text{R}_2\text{HgR}'$  can be made by the reaction  
 of  $\text{R}_2\text{HgCl}$  with  $\text{R}'\text{SnX}_3$ ,  $\text{R}'\text{SnX}_2$  or  $\text{R}'\text{SnX}$  in alk. soln.  
 Reaction investigated in N. S. lab. follow. Diaryl-  
 mercury with  $\text{SnCl}_4$  gives metallic Hg and diarylmethane  
 chloride. In the presence of alk. the products are the  
 aromatic hydromercurates, from Hg and  $(\text{RO})_2\text{SnCl}_2$ .  $\text{Hg-}$   
 $\text{Ph}$  decomposes to give Hg and benzene at  $178^\circ$  in the  
 presence of 50 mm.  $\text{H}_2$  gas.  $\text{Hg}(\text{C}_6\text{H}_5)_2$ , under the  
 same conditions gives bisbenzyl.  $\text{Hg}(\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{COO})_2$ ,  
 like other compds. with the group  $>\text{C}(\text{HgX})_2$  decom-  
 poses, due to an internal oxidation process, to give metallic  
 Hg. The Krasner-Dittmer reaction of diarylmethanes with  
 Al to yield triarylmethanes proceeds much better for  
 Zn and in boiling xylene.  $(p\text{-MeC}_6\text{H}_4)_2\text{Zn}$ ,  $(p\text{-FC}_6\text{H}_4)_2\text{Zn}$ ,  
 $(p\text{-ClC}_6\text{H}_4)_2\text{Zn}$ ,  $(o\text{-C}_6\text{H}_5)_2\text{Zn}$ ,  $(\text{MeNC}_6\text{H}_4)_2\text{Zn}$  were  
 obtained.  $(m\text{-C}_6\text{H}_5)_2\text{Hg}$  failed to react under the same  
 conditions.  $p\text{-AcOH}_2\text{C}_6\text{H}_4\text{NMe}_2$  with  $\text{NaN}_3$  gives  
 the  $\alpha$ -nitroso-substituted amine. The coupling of  $p\text{-}$   
 $\text{ClH}_2\text{C}_6\text{H}_4\text{OH}$  with  $p\text{-ONC}_6\text{H}_4\text{N}_2\text{Cl}$  yields the  $\alpha$ -azo dye  
 $p\text{-[4,2-CH}_2(\text{Me}_2\text{N})\text{C}_6\text{H}_4\text{N}_2\text{N}(\text{Cl})\text{Me}_2\text{NO}_2]$ . F. H. R.

ASB-SCA METALLURGICAL LITERATURE CLASSIFICATION

82-1

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The sequence of "electronegativity" of organic radicals.  
A. N. Nigmatov and K. A. Kocheshkov. *Uchenye Zapiski (Nizh. Sov. Mazhan. Sots. Univ.)* 3, 283-9 (1934); *Chem. Zvesti.* 1935, II, 3493-4.—Hg org. compds. react with  $\text{SnCl}_4$  and  $\text{SnBr}_4$  in 2 ways: (1)  $\text{R.Hg} + \text{SnX}_4$  react with  $\text{SnCl}_4$  and  $\text{SnBr}_4$  in 2 ways: (1)  $\text{R.Hg} + \text{SnX}_4 \rightarrow \text{R.SnX}_3 + \text{Hg}$  and (2)  $\text{R.Hg} + \text{SnX}_4 + 2 \text{KOH} \rightarrow 2 \text{RH} + \text{Hg} + (\text{KXO})_2\text{SnX}_2$ . The tendency to go predominantly in one or the other direction depends upon the character of the radical. If the radicals are arranged in a series according to the yield of  $\text{R.SnX}_3$  by equation (1) or the yield of  $\text{RH}$  by equation (2) the series obtained corresponds essentially with the series of "electronegativity" of Kharasch, although not with that of Rasunov and Koton (*C. A.* 27, 5313-14). W. A. Moore

THE MECHANISM OF THE FORMATION OF MERCURY ORGANIC COMPOUNDS IN REACTION TO DIAMINE COMPOUNDS. A. N. NEMTSYANOV, *Uchenye Zapiski (Kurs. Ser. Khim. Nauk. SSSR-USSR)* 9, 201-5 (1954); *Chem. Zvesti.* 1955, II, 2090; cf. C. A. 50, 19065; 50, 10759.—Expts. are reported to det. the optimum conditions for increasing the yield in Hg-ary. compds. in the reduction of the double salts of phenylmercurous chloride and HgCl<sub>2</sub> with various reducing agents in various solvents. The action of Cu in acetone or AcOEt gave the best yield in PhHgCl (I); SnCl<sub>2</sub> in alc. also gave I. The formation of I by reduction with mercuric Ag in evidence against the intermediate formation of Hg. Moreover, the decompos. of the compds. (RNCH<sub>2</sub>)<sub>2</sub>SnCl<sub>2</sub>, (RNCH<sub>2</sub>)PbCl<sub>2</sub>, and (RNCH<sub>2</sub>)PtCl<sub>2</sub> by Cu powder cannot proceed through the stage of the formation of the free metal. By the action of Cu powder on methylamine-HCl in alc. in the presence of HgCl<sub>2</sub> and AMONO there is formed solely ClCH<sub>2</sub>HgCl, just as in the action of CH<sub>3</sub>N<sub>3</sub> on HgCl<sub>2</sub> (cf. Hellermann, C. A. 26, 4301). AMONO alone, either in the presence or absence of HgCl<sub>2</sub>, has no action on MeNH<sub>2</sub>·HCl in alc.; the latter can be etrd. unchanged from the soln. by Et<sub>2</sub>O. *Diamino-azotic ester* reacts with HgCl<sub>2</sub> according to the equation: 4N<sub>2</sub>CHCO<sub>2</sub>Et + 3HgCl<sub>2</sub> → Hg(C<sub>2</sub>H<sub>4</sub>N<sub>2</sub>CCO<sub>2</sub>Et)<sub>2</sub> (II) + 2C<sub>2</sub>H<sub>4</sub>CO<sub>2</sub>Et + 4N<sub>2</sub>. The compd. II is nonfusible and dissolves only in pyridine. *Marcuribis (diamino ester)*, Hg(N<sub>2</sub>CCO<sub>2</sub>Et)<sub>2</sub>, does not exchange its diamo group for the elements of HgCl<sub>2</sub> in reaction with the latter.

W. A. Moore

W. A. Moore

| 1ST AND 2ND DEGREES                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |  |  |  |  |  |  |  |  |  |  |  | 3RD AND 4TH DEGREES |  |  |  |  |  |  |  |  |  |  |  |
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| PROCESSES AND PROPERTIES INDEX                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |  |  |  |  |  |  |  |  |  |  |  |                     |  |  |  |  |  |  |  |  |  |  |  |
| <p>Simple mercuric cyanide derivatives of phenol. A. N. Nomenzov and E. M. Terepova. J. Gen. Chem. (U. S. S. R.) 4, 654-5 (1934).—<math>m\text{-HOC}_6\text{H}_4\text{HgCl}</math> (I) (Ac. deriv., m. 156-50°) is obtained in 48% yield from <math>m\text{-HOC}_6\text{H}_4\text{N}_3\text{Cl}</math>, <math>\text{HgCl}_2</math> and Cu in EtOH at room temp. I is converted by <math>\text{NaOH}</math> into <math>(m\text{-HOC}_6\text{H}_4)_2\text{Hg}</math> (II) (Ac. deriv., m. 161°), decaying at 215°. The br. ester-izing at 240° <math>\text{I}</math>, melting at 200°, <math>\text{CN}</math>, m. 186-8° and <math>\text{CNS}</math>, m. 172-5°. analogs of I are prepd. by heating II with the corresponding Hg halide. B. C. A.</p> |  |  |  |  |  |  |  |  |  |  |  |                     |  |  |  |  |  |  |  |  |  |  |  |
| <p>REF. 114 METALLURGICAL LITERATURE CLASSIFICATION</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |  |  |  |  |  |  |  |  |  |  |  |                     |  |  |  |  |  |  |  |  |  |  |  |

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| 1ST AND 2ND COPIES                                                                                                                                                                        |  | 3RD AND 4TH COPIES  |  |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|---------------------|--|
| PROCESSING AND PROPERTY INDEX                                                                                                                                                             |  |                     |  |
| BC                                                                                                                                                                                        |  | a-3                 |  |
| <p>Approximate location of the property, as shown on the map, is in the area of the ... (The following text is heavily obscured and mostly illegible due to the quality of the scan.)</p> |  |                     |  |
| ASAC-SCA METALLURGICAL LITERATURE CLASSIFICATION                                                                                                                                          |  |                     |  |
| SOURCE SYMBOL                                                                                                                                                                             |  | SOURCE SYMBOL       |  |
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| COMMON ELEMENTS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |  | PROCEDURES AND REAGENTS |  | 10        |  |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|-------------------------|--|-----------|--|
| <p>Derivatives of allyl esters of phenols mentioned in the<br/>           Russian. A. N. Nemyaynov and R. Kh. Shatzkaya.<br/>           J. Gen. Chem. (U. S. S. R.) 8, 1208-72(1935).—<br/> <math>C_6H_5OC_3H_7Cl</math> (I) was prepd. in 3.5 g. yield (60%) by<br/>           refluxing a mixt. of 8 g. <math>\alpha</math>-NaOC<math>_3H_7</math> (II) in 20 cc.<br/>           Me<math>_2</math>CO with 6 g. allyl bromide (III) for 7 hrs. A pro-<br/>           longed heating gave <math>\alpha</math>-(<math>C_6H_5OC_3H_7</math>)<math>_2</math> (IV), m. 50.5<br/>           (0.5°). IV was also obtained by substituting allyl chloride<br/>           for III in the above reaction, and by treating 1 g. I with<br/>           1 g. SnCl<math>_4</math> in 20% NaOH. (<math>C_6H_5OC_3H_7</math>)<math>_2</math> (IV), m.<br/>           121-1.5°, was obtained (1) by treating 30 g. II in 40 g.<br/>           C<math>_6</math>H<math>_5</math>N at -10° with 11.2 g. III; (2) by mixing in the<br/>           cold 3 g. H<math>_2</math>O in C<math>_6</math>H<math>_5</math>N (mtd.) with an equal vol. of III;<br/>           and (3) from 1,2-<math>HOOC_3H_7Cl</math> in C<math>_6</math>H<math>_5</math>N with III.<br/> <math>p</math>-<math>C_6H_4OC_3H_7Cl</math> (V), m. 101-1.5°, was obtained in<br/>           21.8 g. yield (57%) by treating an emulsion of 15 g.<br/>           PhOC<math>_3H_7</math>, 9 cc. of 40% AcOH and 37 cc. H<math>_2</math>O with 6.5 g.<br/>           H<math>_2</math>O in form of a paste, pouring the hot mixt. into a cool-<br/>           ing soln. of 80 g. NaCl, boiling for 2-3 min. and allowing<br/>           the mixt. to cool. V, treated with Na stannate as above,<br/>           gave <math>p</math>-(<math>C_6H_4OC_3H_7</math>)<math>_2</math> (VI), m. 108.5-10°. <math>C_6H_5OC_3H_7</math><br/>           and H<math>_2</math>O by the method described for the prepn. of V. The<br/>           structures of some of these compds. are being investigated.<br/>           Chas. Blanc</p> |  |                         |  |           |  |
| 458-114 METALLURGICAL LITERATURE CLASSIFICATION                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |  |                         |  |           |  |
| RECORD SYMBOL                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |  | RECORDS MAY ONLY BE     |  | REVISIONS |  |
| RECORD NO.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |  | RECORDS MAY ONLY BE     |  | REVISIONS |  |



NESMEJANOW, A. N.

"Sur l'obtention des 2 -et 4-allylresorcines et leurs transformation en 1-chloremercure-methyl 1-2 dihydrooxybenzofuranes". Nesmejanow, A. N. et Zarewitch, T. S. (p. 140)

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1936, Volume 6, No. 1

CH

Double salts of crystallization chlorides and chlorides of heavy metals. K. A. Kucharskii and A. N. Nersisyan. *J. Gen. Chem.* (U.S.S.R.), 6, 144-46 (1936).  
 $\text{FeCl}_3 \cdot \text{e-MgCl}_2 \cdot \text{H}_2\text{O}$  (I),  $\text{e-MgCl}_2 \cdot \text{H}_2\text{O}$ ,  $\text{e-CH}_3\text{COONa} \cdot \text{H}_2\text{O}$  (II),  $\text{e-HOOCCH}_2\text{CH}_2\text{CH}_2\text{COONa}$ ,  $\text{e-MgCl}_2 \cdot \text{H}_2\text{O}$ ,  $\text{e-CH}_3\text{COONa} \cdot \text{H}_2\text{O}$ ,  $\text{e-CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COONa}$ ,  $\text{e-MgCl}_2 \cdot \text{H}_2\text{O}$ ,  $\text{e-CH}_3\text{COONa} \cdot \text{H}_2\text{O}$ ,  $\text{e-CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COONa}$  (III),  $\text{e-MgCl}_2 \cdot \text{H}_2\text{O}$ ,  $\text{e-CH}_3\text{COONa} \cdot \text{H}_2\text{O}$ ,  $\text{e-CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COONa}$  were caused to react with  $\text{ZnCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{TiCl}_4$ ,  $\text{SnCl}_4$ ,  $\text{PbCl}_2$ ,  $\text{BiCl}_3$ ,  $\text{AsCl}_3$ ,  $\text{PbCl}_4$  and  $\text{FeCl}_4$ . The double salts were prepd. by pouring the metal chloride in concd.  $\text{HCl}$  into 1%  $\text{N RN}_4\text{Cl}$  in 5%  $\text{N HCl}$  prepd. by dissolution into water of  $\text{NaOH}$  of 1 mol.  $\text{RNH}_2$  in 300 cc. concd.  $\text{HCl}$  and 300 g. ice and adding enough 8%  $\text{N HCl}$  to make 1 l. The pptd. salts (the  $\text{Zn}$  and  $\text{Cd}$  salts) were sometimes ppt. only after long cooling at  $-15^\circ$ ) were filtered off, washed with cold 5%  $\text{HCl}$ , etc. and  $\text{Et}_2\text{O}$  and dried in air. The compn. of the double salt was usually independent of the relative proportions of reactants. Usually were taken for each mol. of  $\text{RN}_4\text{Cl}$ , 0.5 mol. of  $\text{TiCl}_4$ ,  $\text{ZnCl}_2$ ,  $\text{CoCl}_2$ ,  $\text{SnCl}_4$ ,  $\text{PbCl}_4$  and  $\text{PbCl}_2$ , and 1 mol. of  $\text{TiCl}_4$ ,  $\text{BiCl}_3$  and  $\text{AsCl}_3$ , and a large excess of  $\text{FeCl}_3$  (otherwise the Fe salts were not pptd.). With  $\text{TiCl}_4$  and  $\text{BiCl}_3$  the proportions 1 mol. metal chloride and 2 mols.  $\text{RN}_4\text{Cl}$  and 1 mol.  $\text{RN}_4\text{Cl}$  and 1.5 mols. metal chloride were likewise used. Concns. (M) of the metal chlorides in  $\text{HCl}$ :  $\text{ZnCl}_2$ , 0.05;  $\text{CoCl}_2$ , 2.5 M;  $\text{TiCl}_4$ , 2 M;  $\text{SnCl}_4$ , 2.5 M;  $\text{PbCl}_2$ , 0.3 M;  $\text{BiCl}_3$ , 3 M;  $\text{PbCl}_4$ , 1 M;  $\text{AsCl}_3$ , 1 M;  $\text{FeCl}_3$ , satd. The concn. of the double salts of  $\text{As}$ ,  $\text{Zn}$ ,  $\text{Sn}$ ,  $\text{Pb}$ , satd.

Fe and Fe was independent of the structure of R which, with the other metals, the nature of R affected the complex. Au, Zn and Fe had coordination no. 4; Sn, Pt and Pb had 6. The coordination no. of Cd and Hg varied from 3 to 4, and that of Ti and Bi from 4 to 6. The complexes gave salts with the anion, no. of  $\text{RNC}_4\text{R}'$  moles, being the only compound to give with  $\text{CdCl}_2$  the type  $\text{RNC}_4\text{R}'_2\text{CdCl}_2$  with all proportions of reactants. If gave 2 Hg, Cd, Cl with  $\text{BiCl}_3$  only 2 Hg,  $\text{BiCl}_3$ .  $\text{TiCl}_4$  gave only 1 Hg,  $\text{TiCl}_4$ . Both Hg,  $\text{HgCl}_2$

and 2 H.HgCl<sub>2</sub> were formed. III gave salts with max. coordination no. of the metal, except that the 2 H.HgCl<sub>2</sub> was contaminated with some H.HgCl<sub>2</sub>. III was the only R<sub>2</sub>NCl to give a pure salt of the type (R<sub>2</sub>NCl)<sub>2</sub>TiCl<sub>4</sub> and which did not give R<sub>2</sub>NCl.TiCl<sub>4</sub>. For the remaining compds. the influence of R is less pronounced. The soly. in many solvents and the decompn. temp. of each double salt are given. These properties are of interest in connection with the formation of organometallic compds. from the double salts. The soly. was affected chiefly by the nature of the metal component; the decompn. temp., by the nature of R. The presence of neg. substituents in the Ph nucleus made for increased thermal stability, the *p*-derivs. being most stable. The salts of Pt, Cd, Hg and Sn were the most stable. The compn. of each double salt and a review of earlier literature are given. L. W. B.

Full trans. available in M.

| 1ST AND 2ND OFFICE                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |  |  |  |  |  |  |  |  |  | PROCEDURE AND PROPERTIES INDEX |  |  |  |  |  |  |  |  |  | MR. AND MR. CAPTAIN |  |  |  |  |  |  |  |  |  |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|--|--|--|--|--|--|--|--|--------------------------------|--|--|--|--|--|--|--|--|--|---------------------|--|--|--|--|--|--|--|--|--|
| BC                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |  |  |  |  |  |  |  |  |  |                                |  |  |  |  |  |  |  |  |  | L-3                 |  |  |  |  |  |  |  |  |  |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |  |  |  |  |  |  |  |  |  |                                |  |  |  |  |  |  |  |  |  |                     |  |  |  |  |  |  |  |  |  |
| <p>Extraction of organic tin compounds from<br/>           chloroformate. K. A. Kabanov, A. N.<br/>           Kabanov, and V. A. Kabanov (J. Gen. Chem.<br/>           USSR, 1964, 3, 102-103). Contains organotin<br/>           compounds, some with Sn in boiling EtOAc, as<br/>           follows: <math>(\text{C}_2\text{H}_5)_2\text{SnCl}_2</math>, <math>(\text{C}_2\text{H}_5)_4\text{Sn}</math>, <math>(\text{C}_2\text{H}_5)_3\text{SnO}-</math><br/> <math>\text{C}_6\text{H}_5</math>, <math>(\text{C}_2\text{H}_5)_2\text{Sn}(\text{C}_6\text{H}_5)_2</math>, <math>(\text{C}_2\text{H}_5)_2\text{Sn}(\text{C}_6\text{H}_5)_2</math>. When<br/> <math>\text{EtOAc}</math> is the solvent, the product is <math>(\text{C}_2\text{H}_5)_2\text{SnCl}_2</math>, m.p.<br/>           115°, when <math>\text{EtOAc}</math> is the solvent, <math>\text{p}-\text{C}_6\text{H}_4</math><br/> <math>\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{SnCl}_2</math>, m.p. 104°, is obtained. R. T.</p> |  |  |  |  |  |  |  |  |  |                                |  |  |  |  |  |  |  |  |  |                     |  |  |  |  |  |  |  |  |  |
| <p>ASS. 5.4 METALLURGICAL LITERATURE CLASSIFICATION</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |  |  |  |  |  |  |  |  |  |                                |  |  |  |  |  |  |  |  |  |                     |  |  |  |  |  |  |  |  |  |
| FROM STUDENT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |  |  |  |  |  |  |  |  |  | FROM STUDENT                   |  |  |  |  |  |  |  |  |  | FROM STUDENT        |  |  |  |  |  |  |  |  |  |
| LITERATURE                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |  |  |  |  |  |  |  |  |  | LITERATURE                     |  |  |  |  |  |  |  |  |  | LITERATURE          |  |  |  |  |  |  |  |  |  |

**CIA-RDP86-00513R0011366200**

| PROCEDURES AND PROPERTIES INDEX                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |  |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|
| <p>(A) Structure of products of addition of mercury salts to unsaturated compounds by the arylation method. A. N. MAMZANOV, and R. C. FREIDMAN. (B) Reaction of dimethylmercury with <math>\beta</math>-bromomethyl alcohol, and the structure of the products of addition of mercury salts to olefins. R. C. FREIDMAN, A. N. MAMZANOV, and F. A. TOKAROVA (J. Gen. Chem. Russ., 1957, 7, 43-50, 252-255). (A) <math>\text{OH-CH}_2\text{-CH}_2\text{-HgBr}</math> (I) in <math>\text{C}_6\text{H}_6</math> and <math>\text{PhCOO}</math> yield <math>\beta</math>-bromomethyl phosphonate (II), m.p. 124-125° (decomp.). (I) in aq. alcoholic KOH and di-<i>p</i>-tolylchloro-stannane afford <math>\beta</math>-hydroxyethyl-<i>p</i>-tolylmercury (III), m.p. 55-56-57.5°. <math>\text{Hg(OAc)}_2</math> and cyclohexane (IV) in <math>\text{H}_2\text{O}</math> yield 2-acetomercurycyclohexanol, m.p. 112-5-113.5°, which reacts with <math>\text{NaPh}_2\text{Cl}_2</math> (V) in <math>\text{EtOH-KOH}</math>, at the b.p., to afford 2-phenylmercurycyclohexanol (VI), m.p. 101-102°. <math>\text{Hg(OAc)}_2</math> and (IV) in <math>\text{EtOH}</math> give 1-ethyl-2-acetomercurycyclohexane, m.p. 78°, converted by boiling with NaOH and (V) in <math>\text{EtOH}</math> into <math>\text{Hg}</math> phenyl 2-ethoxycyclohexyl (VII). 1-Chloromercurimethyl-1:2-dihydrobenzofuran, NaOH, and (V) in <math>\text{EtOH}</math>, at the b.p., afford 1-phenylmercurimethyl-1:2-dihydrobenzofuran, m.p. 60-61°. This,</p> |  |
| <p>similarly to (II), (III), (VI), and (VII), is decomposed by 15% HCl, with production of unsaturated hydrocarbon and <math>\text{Hg}</math> aryl chloride. The reactions support the structure given above for (I), rather than one involving residual valencies, of the type <math>\text{C}_6\text{H}_5\text{HgBrOH}</math>. (B) (I) and <math>\text{CH}_3\text{N}_3</math> in <math>\text{Et}_2\text{O}</math> yield <math>\beta</math>-bromomethylmercurimethyl alcohol, which decomposes at room temp. with production of <math>\text{C}_2\text{H}_4</math>, <math>\text{Hg}</math>, bromomethylmercuric bromide (VIII), m.p. 124-125°, <math>\text{CH}_2\text{O}</math>, and <math>\text{N}_2</math>. <math>\text{HgBr}_2</math> and <math>\text{CH}_3\text{N}_3</math> in <math>\text{Et}_2\text{O}</math> yield (VIII) and <math>\text{Hg}</math> dibromodimethyl, m.p. 62-43°. (VIII) and aq. NaOH yield <math>\text{Hg}</math>, <math>\text{CH}_2\text{O}</math>, and <math>\text{HBr}</math>. R. T.</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |  |
| <p>658-516 METALLURGICAL LITERATURE CLASSIFICATION</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |  |
| <p>INDEX SYMBOLS</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |  |
| <p>SYMBOLS</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |  |

| 1ST AND 2ND OFFERS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |  | PROCESSED AND PROPERTY INDEX |  | 3RD AND 4TH OFFERS |  |
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| <p><i>Reduction of organic mercury compounds by aliphatic</i><br/> <i>in compounds as a synthetic method for aromatic substitu-</i><br/> <i>tion substituted in the (benzene) nucleus with hydroxy-</i><br/> <i>and amino groups. A. N. Nemayunov, K. A. Kochen-</i><br/> <i>kov and V. P. Puzrevich. 1957. 1700. (U. S. S. R.) 7,</i><br/> <i>115 21 (1957); cf. C. A. 28, 927, 2702; 30, 1670. The</i><br/> <i>difficulties of obtaining aromatic Sn compounds of the type</i><br/> <i>R<sub>2</sub>SnX<sub>2</sub> and R<sub>2</sub>SnX from corresponding R<sub>2</sub>HgX and R<sub>2</sub>Hg</i><br/> <i>compds., contg. OH and NH<sub>2</sub> groups in the ring in the <math>\alpha</math>-</i><br/> <i>and <math>\beta</math>-positions to the Hg atom (cf. C. A. 28, 8875),</i><br/> <i>are overcome by substituting aliphatic Sn compounds of the</i><br/> <i>types R<sub>2</sub>Sn and (R<sub>2</sub>Sn)<sub>2</sub> for R<sub>2</sub>Hg and R<sub>2</sub>Hg<sub>2</sub> in the reac-</i><br/> <i>tion. R<sub>2</sub>Sn (I) and (R<sub>2</sub>Sn)<sub>2</sub> (II) are capable of reducing</i><br/> <i>Hg compounds, forming corresponding stannanes: I +</i><br/> <i>HgCl<sub>2</sub> <math>\rightarrow</math> R<sub>2</sub>SnCl<sub>2</sub> + Hg; II + HgCl<sub>2</sub> <math>\rightarrow</math> 2 R<sub>2</sub>SnCl +</i><br/> <i>Hg. Somewhat more slowly proceed the reactions: II +</i><br/> <i>PhHgCl <math>\rightarrow</math> R<sub>2</sub>SnCl + PhSnR<sub>2</sub> + Hg; II + PhHg<sub>2</sub> <math>\rightarrow</math> 2</i><br/> <i>PhSnR<sub>2</sub> + Hg; I + PhHg <math>\rightarrow</math> Ph<sub>2</sub>SnR<sub>2</sub> + Hg. The</i><br/> <i>introduction of OH and NH<sub>2</sub> groups into the ring in the <math>\alpha</math>-</i><br/> <i>and <math>\beta</math>-positions to the Hg atom results in a greater reactivity:</i><br/> <i>II + (p-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Hg (III) <math>\rightarrow</math> 2 p-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>SnR<sub>2</sub> (IV) +</i><br/> <i>Hg; II + (o-HOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Hg (V) <math>\rightarrow</math> 2 o-HOC<sub>6</sub>H<sub>4</sub>SnR<sub>2</sub> (VI)</i><br/> <i>(VI) + Hg. II, b. 160°, resulted in 70% yield from</i><br/> <i>40 g. R<sub>2</sub>SnCl (cf. C. A. 28, 2325), 5 g. of powd. Na and</i><br/> <i>80 cc. iso-AmOH by digesting the mixt. in an oil bath at</i><br/> <i>180° for 5 hrs. and distg. in a N atm. An equimol</i><br/> <i>mixt. of II and HgCl<sub>2</sub> heated at 150° for 30 min. gave 74%</i><br/> <i>R<sub>2</sub>SnCl. This with K<sub>2</sub>SO<sub>4</sub> gave R<sub>2</sub>SnCl<sub>2</sub>, m. 43-4°</i><br/> <i>II with PhHgCl at 150-160° for 3 hrs. resulted in 30%</i><br/> <i>Ph<sub>2</sub>SnR<sub>2</sub>, b. 113-14°. II with PhHg at 160° for 7 hrs.</i><br/> <i>gave 40% Ph<sub>2</sub>SnR<sub>2</sub> (60% Hg). II with III digested on a</i><br/> <i>water bath for 30 min. and then in an oil bath at 150-170°</i><br/> <i>for 5 hrs. gave IV, b. 172-3°, d<sub>20</sub> 1.2425, n<sub>D</sub> 1.561. IV</i><br/> <i>with HgCl<sub>2</sub> in alc. formed 65% p-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>HgCl, m.</i><br/> <i>215°. The alc. filtrate treated with K<sub>2</sub>SO<sub>4</sub> and extd. with</i><br/> <i>Et<sub>2</sub>O gave R<sub>2</sub>SnOH<sub>2</sub>. This with Ac<sub>2</sub>SO<sub>4</sub> gave R<sub>2</sub>SnCl<sub>2</sub>Ac.</i><br/> <i>m. 130-1°. If in CHCl<sub>3</sub> was treated with H<sub>2</sub> at 0°, the</i><br/> <i>solvent was distd. off and the residue was dissolved in Et<sub>2</sub>O.</i><br/> <i>After purg. R<sub>2</sub>SnCl<sub>2</sub> with H<sub>2</sub>, the filtrate was evapor.</i><br/> <i>giving p-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>Hg, m. 55° (pure ether). II with V</i><br/> <i>at 130° for 2 hrs. afforded nearly 100% VI, b. 167-168°,</i><br/> <i>d<sub>20</sub> 1.2220, n<sub>D</sub> 1.5377. Treated with HgCl<sub>2</sub> it gave o-</i><br/> <i>HOC<sub>6</sub>H<sub>4</sub>HgCl. Treating I with HgCl<sub>2</sub> (exothermic reac-</i><br/> <i>tion) resulted in 80% Et<sub>2</sub>SnCl<sub>2</sub>, b. 84°, and 100% Hg.</i><br/> <i>I with PhHg at 150° for 30 min. gave 60% Ph<sub>2</sub>SnR<sub>2</sub>, b.</i><br/> <i>184-5°.</i><br/> <i>Chas. Blane</i></p> |  |                              |  |                    |  |
| <p>ASD-514 METALLURGICAL LITERATURE CLASSIFICATION</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |  |                              |  |                    |  |
| <p>STOCK SYMBOL</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |  |                              |  |                    |  |
| <p>RESEARCH ONE AND TWO</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |  |                              |  |                    |  |

NESMELANOW, A. N.

"Sur la reaction du diazomethane avec l'etanolmercuro-bromure et sur la structure des produits de la fixation des sels sur mercure sur les olefines."

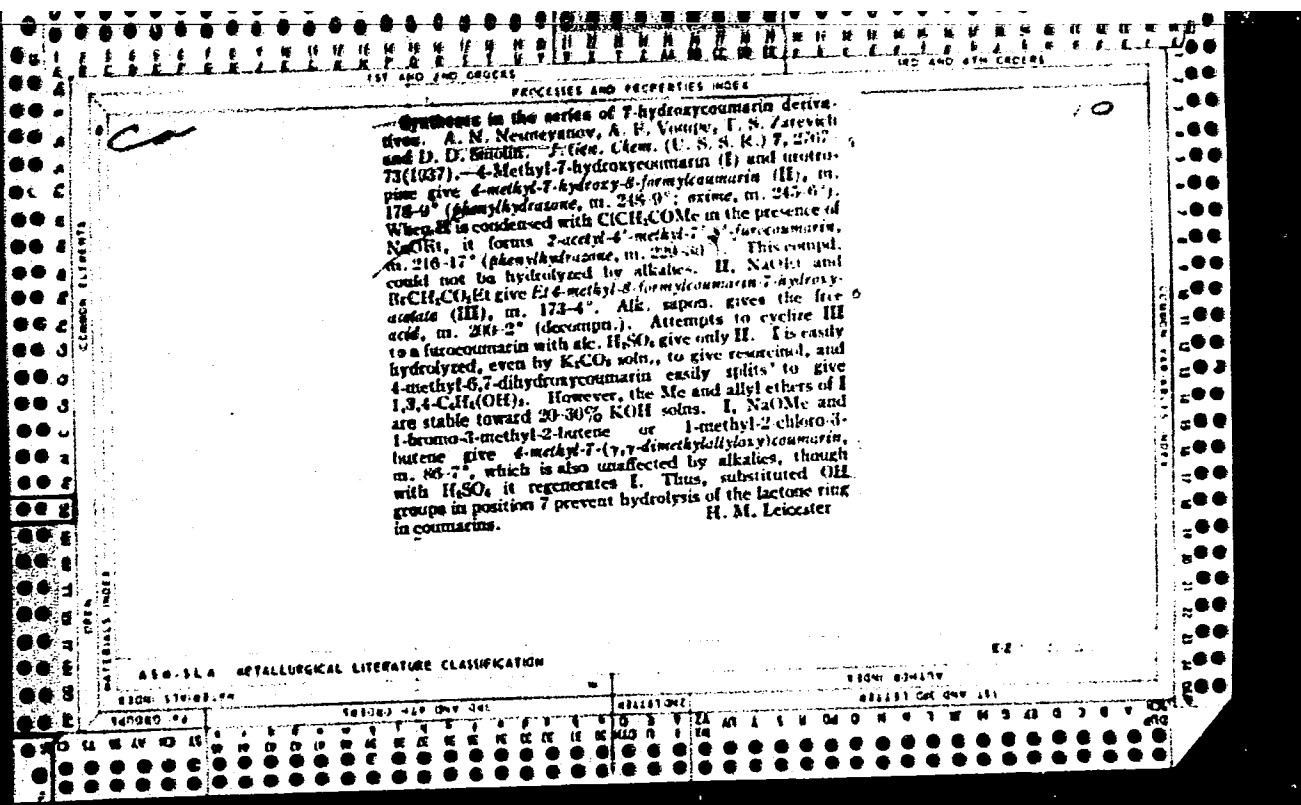
Freidline, R. Ch., Nesmelanow, A. N., et Tokarewa, F. A. (p. 262.)

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1937, Volume 7, No.1

| COMMON ELEMENTS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |  | PROCESSES AND PROPERTIES INDEX |  |
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| <p><b>Diphenylcadmate.</b> A. N. Nesmerakov and L. G. Makarova. <i>J. Gen. Chem. (U. S. S. R.)</i> 7, 2640-51 (1937).—When <math>\text{CdBr}_2</math> is treated with an excess of <math>\text{LiPh}</math> in <math>\text{Et}_2\text{O}</math> in an atm. of dry <math>\text{N}_2</math> and the evapd. reaction mixt. is extd. with <math>\text{C}_6\text{H}_6</math>, <math>\text{Ph}_2\text{Cd}</math>, m. <math>173-4^\circ</math>, can be sepd. It is very easily decompd. by <math>\text{O}</math> and moist air. It reacts with <math>\text{HgCl}_2</math>, <math>\text{SnCl}_2</math> and <math>\text{SbCl}_3</math> to give the completely phenylated org.-metallic compds. but it does not react with <math>\text{PbCl}_2</math>. With <math>\text{PhI}_2</math> it gives <math>\text{PhI}_2\text{Cl}</math>. With <math>\text{H}_2\text{O}</math>, alca., amines, <math>\text{NH}_3</math>, <math>\text{C}_6\text{H}_6</math> and fluorene it is decompd. to <math>\text{C}_6\text{H}_6</math>. With <math>\text{NO}</math> it forms <math>\text{PhN:NNO}</math>. It does not react with <math>\text{CO}_2</math> or <math>\text{CHCl}_3</math>. H. M. Leicester</p> |  |                                |  |
| <p>ADD-524 METALLURGICAL LITERATURE CLASSIFICATION</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |  |                                |  |
| SIGNATURE                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |  | REMARKS                        |  |
| <p>SEARCHED <input type="checkbox"/> INDEXED <input type="checkbox"/></p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |  | <p>REMARKS</p>                 |  |



| CROSS INDEX                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |  | PROCESS AND PROPERTIES INDEX |  | CROSS INDEX |  |
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| <p><i>Co</i></p> <p>Mercury organic comp. 4g. XV. The structure of the addition compounds of mercury salts with styrene and <i>n</i>-methylstyrene. A. N. Nigmatov, and R. Kh. Proskina. <i>J. Gen. Chem. (U. S. S. R.)</i> 7, 2748-51 (1947); cf. C. A. 40, 8156. When equimol. amts. of styrene and <math>Hg(OAc)_2</math> react in <math>H_2O</math> soln., <math>PhCH(OH)CH_2HgOAc</math> (I), m. 77-8° (decolor.), is formed. With Na-Hg this is reduced to <math>PhCH(OH)Me</math>. I and NaCl form the corresponding mercurichloride, m. 95-6°, and with NaBr it gives the bromide, m. 102-3°. When excess <math>Hg</math> salts are used, compds. of the type of <math>3(PhCH(OH)CH_2HgCl) \cdot HgCl_2</math> are formed. <math>PhC(CH_3)Cl_2</math> and <math>Hg(OAc)_2</math> give <math>PhC(OH)(CH_3)CH_2HgOAc</math> (II), m. 101-2°, which is reduced to <math>PhC(CH_3)CH_2OH</math>. The chloride of II is a liquid, and the bromide m. 45-6°. The compd. obtained by Manchot (C. A. 19, 508) from styryl Et ether and <math>Hg(OAc)_2</math> probably has the structure <math>PhCH(HgOAc)CH_2(OH)OEt</math>.</p> <p>H. M. Leicester</p> |  |                              |  |             |  |
| <p>450-51A METALLURGICAL LITERATURE CLASSIFICATION</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |  |                              |  |             |  |
| <p>RECORD SYMBOLS</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |  |                              |  |             |  |
| <p>RECORDS</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |  |                              |  |             |  |
| <p>RECORDS</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |  |                              |  |             |  |



Organic tin compounds of the type  $Ar_3SnX$ , with a carbonyl group in the benzene nucleus. I. T. Rikin, A. N. Neumayr and K. A. Korshakov. *J. Gen. Chem.* (U.S.S.R.) 3, 38-41 (1933); cf. K. and N., C. A. 28, 2702, 2975.  $(p\text{-EtOCC}_6\text{H}_4)_3\text{SnX}$  (X = halogen) were obtained from  $(\text{EtOCC}_6\text{H}_4)_2\text{Hg}$  with  $\text{SnX}_2$ . The reaction is possible with  $\text{SnCl}_4$  in abs. alc. and  $\text{Me}_2\text{CO}$  and with  $\text{SnBr}_4$  in alc. (cf. N. and K., C. A. 28, 927). Satisfactory yields were obtained without the use of a solvent by heating the mixt. on a water bath for about 1 hr. By this method 71% diphenyldichlorostannane,  $\text{Ph}_2\text{SnCl}_2$ , m.  $42^\circ$ , was obtained. This (2 g.) in 15-20 ml. alc. with unstd.  $\text{H}_2\text{S}$  in 6% alc. KOH gave 74% diphenyldichlorostannane,  $\text{Ph}_2\text{SnBr}_2$ , m.  $183-4^\circ$ . Dicarboethoxyphenyldichlorostannane,  $(p\text{-EtOCC}_6\text{H}_4)_2\text{SnCl}_2$  (I), m.  $102-3^\circ$  (83% yield), from 0.006 mol.  $(p\text{-EtOCC}_6\text{H}_4)_2\text{Hg}$  and 0.0153 mol.  $\text{SnCl}_4$ . This with  $\text{HgCl}_2$  in alc. gave nearly 100%  $\text{EtOCC}_6\text{H}_4\text{HgCl}$ , m.  $223-4^\circ$ , (cf. N. and Makarov, C. A. 26, 4028). I (0.15 mol.) condensed with 0.10 mol.  $\text{PhMgBr}$  in  $\text{Et}_2\text{O}$  and the product decomposed with aq.  $\text{NH}_4\text{Cl}$  gave 72% of a triphenylcar-

binol deriv. of  $\text{Sn}$ ,  $\text{Ph}_3\text{Sn}(\text{PhC}_6\text{H}_4\text{OH})$ , m.  $205-6^\circ$ . I gave 89.9% dicarboethoxyphenyldichlorostannane,  $(\text{EtOCC}_6\text{H}_4)_2\text{SnBr}_2$ , m.  $141.5-2.5^\circ$ . Salts with  $(\text{EtOCC}_6\text{H}_4)_2\text{Hg}$  at  $225-35^\circ$  gave 57% dicarboethoxyphenyldichlorostannane (II), m.  $69-7.5^\circ$ . This in  $\text{Me}_2\text{CO}$  when hydrolyzed with 12%  $\text{NH}_4\text{OH}$  gave nearly 100% dicarboethoxyphenyldichlorostannane,  $(\text{EtOCC}_6\text{H}_4)_2\text{SnBr}_2$ , does not m.  $100^\circ$ . Salts with none  $(\text{EtOCC}_6\text{H}_4)_2\text{Hg}$  in dry  $\text{Me}_2\text{CO}$  gave not II, but  $\text{EtOCC}_6\text{H}_4\text{HgCl}$ , m.  $211-12^\circ$ , (cf. N. and K., loc. cit.). The  $p\text{-EtOCC}_6\text{H}_4\text{HgCl}$  formed an oil, which did not crystallize after standing for several months. This oil and II when treated in hot alc. with 8-hydroxyquinoline gave the identical condensation product,  $(\text{EtOCC}_6\text{H}_4)_2\text{Sn}(\text{OC}_6\text{H}_4\text{N})_2$ , m.  $216-17^\circ$ . A mixt. of the variously obtained compds. gave no depression of the m. p. Fifteen references. (Has. Hahn)

| 1ST AND 2ND COLUMNS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |  |  |  |  |  |  |  |  |  |  |  | 3RD AND 4TH COLUMNS                                                                                                                                               |  |  |  |  |  |  |  |  |  |  |  |
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| PROCESSES AND PROPERTIES INDEX                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |  |  |  |  |  |  |  |  |  |  |  |                                                                                                                                                                   |  |  |  |  |  |  |  |  |  |  |  |
| <div style="position: relative; height: 100px;"> <span style="position: absolute; top: 10px; left: 10px; font-size: 2em; font-family: cursive;">ca</span> </div>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |  |  |  |  |  |  |  |  |  |  |  | <div style="position: relative; height: 100px;"> <span style="position: absolute; top: 10px; right: 10px; font-size: 2em; font-family: cursive;">10</span> </div> |  |  |  |  |  |  |  |  |  |  |  |
| <p>Preparation of diazo compounds by means of organometallic compounds. L. G. Makarov and A. M. Nemyaynov. <i>J. Gen. Chem.</i> (U. S. S. R.) 9, 771-9(1939).—Based on the assumption that the reaction mechanism between <math>N_2O_2</math> (I) and organometallics (II) + <math>2N_2</math> (III) according to the equations: <math>Ph_3M + 2I \rightarrow 2PhNO + M(NO_2)_2</math>, and <math>PhNO + 2III \rightarrow PhN_2NO_2</math> (IV), expts. were carried out with I and III simultaneously and the following organometallic compds.: <math>Ph_3Hg</math>, <math>Ph_3Sn</math>, <math>Ph_3SnCl</math>, <math>Ph_3SnCl_2</math>, <math>Ph_3SnCl_3</math>, <math>Ph_3Pb</math>, <math>Ph_3PbCl</math> and <math>Ph_3Bi</math>. The yields of IV were 45%, 40%, 48%, 49%, 50%, quant., 50%, 54%, resp., as compared with 21%, not investigated, 8%, 5%, 10%, 24%, 18%, 10%, resp., when I was used alone. <math>Ph_3TiCl</math> reacts with I with the formation of 8% IV. <math>PhMgBr</math> (V) yields 15% IV on reaction with I. When 1 mol. <math>ZnCl_2</math> is added to 3 mols. V, the yield is increased to 20%. About the same increase is observed after the addn. of <math>CdBr_2</math>. In the 2 latter cases the simultaneous addn. of III did not increase the yield. From the reaction products of <math>Ph_3Zn</math> with I + III, and of <math>Ph_3Li</math>, <math>Ph_3As</math> and <math>Ph_3Sb</math>, resp., with I, phenyldiazonium compds. could not be isolated. <math>Ph_3Si</math> and <math>Ph_3PbCl_2</math> did not react with I. Gertrude Berend</p> |  |  |  |  |  |  |  |  |  |  |  |                                                                                                                                                                   |  |  |  |  |  |  |  |  |  |  |  |
| ASD-51A METALLURGICAL LITERATURE CLASSIFICATION                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |  |  |  |  |  |  |  |  |  |  |  |                                                                                                                                                                   |  |  |  |  |  |  |  |  |  |  |  |
| 1ST COLUMN                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |  |  |  |  |  |  |  |  |  |  |  | 2ND COLUMN                                                                                                                                                        |  |  |  |  |  |  |  |  |  |  |  |
| 3RD COLUMN                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |  |  |  |  |  |  |  |  |  |  |  | 4TH COLUMN                                                                                                                                                        |  |  |  |  |  |  |  |  |  |  |  |

III AND THE ORDER

VII AND THE ORDER

CA

Carbonyls of the metals of the sixth group of the periodic system. I. K. A. Kocheshkov, A. N. Nemeyanov, M. N. Nadj, I. M. Rosinskaya and L. M. Borisova. *Compt. rend. acad. sci. U. R. S. S.* 26, 54-7(1940)(in English).—In the prepn. of the hexacarbonyls of Cr, Mo and W from the chlorides together with CO and the Grignard reagent in an ether-benzene medium it is suggested that the Grignard reagent merely acts as a reducing agent and that no metal organic intermediates are formed. The hexacarbonyls were successfully prepd. by using Zn or Fe dust, as reducing agent, in place of the Grignard reagent. Higher yields of the W carbonyl (10-11%) were obtained by using dry ether as a medium and of the Mo carbonyl (10-11%) by using dry acetone in place of the ether-benzene. Yields were highest when the reaction mixt. was maintained between -10° and 0°. This method yields very pure products. II. K. N. Anisimov and A. N. Nemeyanov. *Ibid.* 38-9(in English). The yields of the hexacarbonyls can be increased by carrying out the reaction in an autoclave at increased pressure. With an initial pressure of 100-120 atm. the yield of W carbonyl was 70%; with initial pressure of 90 atm. the yield of Mo carbonyl was 10%. Temp. has little effect at these pressures, the reactions being carried out at room temp. Use of WOCl<sub>5</sub> as starting material results in 27% yield. WO<sub>3</sub> gave no reaction. CrCl<sub>3</sub> in alcohol gave no reaction by this method but with phenylmagnesium bromide in ether and with CO pressure of 115 atm. a 26% yield was obtained. No carbonyl of Cr could be obtained by using CrCl<sub>3</sub> (aq. soln.) with CO (about 110 atm. pressure) in the presence of Zn. H. A. Friedman

ASS. 544 METALLURGICAL LITERATURE CLASSIFICATION

RECORD STRUCTURE      REFERENCE ONE ONLY REC      REFERENCE ONE ONLY REC

| 1ST AND 2ND DDD(EE)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |  |  |  |  |  |  |  |  |  |  |  | 3RD AND 4TH DDD(EE) |  |  |  |  |  |  |  |  |  |  |  |
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| PROCESSES AND PROPERTIES INDEX                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |  |  |  |  |  |  |  |  |  |  |  |                     |  |  |  |  |  |  |  |  |  |  |  |
| <p><b>CA</b></p> <p>Structure of addition products of metal halides and unsaturated compounds. R. Kh. Freidlin and A. N. Nemeyanov. <i>Compt. rend. acad. sci. U. R. S. S.</i> 26, 66-67(1949)(in English). The addn. product of HgCl<sub>2</sub> and C<sub>6</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>5</sub>.HgCl, can be prep. easily by satg. (for 3 hrs.) a soln. of 7.9 g. HgCl<sub>2</sub> in 75 ml. HCl (1:1) with C<sub>6</sub>H<sub>6</sub>. The yield is 3.8-3.9 g.; m. p. 122-4° (decomps.). Addn. of NH<sub>3</sub> to a CHCl<sub>3</sub> soln. of this product yields (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>HgCl<sub>2</sub> which, after rectifyg., forms a mixt. of pure ether and ether, m. pt. 61-62°. These compds. react with Ph<sub>3</sub>I<sub>2</sub>C<sub>2</sub> to form C<sub>6</sub>H<sub>5</sub>(Ph)<sub>2</sub>C<sub>2</sub> and Ph<sub>3</sub>C<sub>2</sub>; with Cl<sub>2</sub>N<sub>2</sub> to form ClCN.HgCl<sub>2</sub>·N and C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>; and with Ph<sub>3</sub>P to form C<sub>6</sub>H<sub>5</sub> and (Ph<sub>3</sub>P)<sub>2</sub>HgCl<sub>2</sub>. These products are the same as those formed by permitting free HgCl<sub>2</sub> to react with the resp. reagents. Acting as true organomercuric compds. these substances also react with I in ether to yield HgClI + C<sub>6</sub>H<sub>5</sub>CHI. This quality in chem. behavior is explained by partial disocc., tautomerism of the at. and mol. forms, and a hybrid-resonance: C<sub>6</sub>H<sub>5</sub>:CHHgCl ↔ C<sub>6</sub>H<sub>5</sub>.HgCl. A study of the Raman spectra is proposed.<br/>H. A. Frediani</p> |  |  |  |  |  |  |  |  |  |  |  | <p><b>10</b></p>    |  |  |  |  |  |  |  |  |  |  |  |
| A.S.M.-S.A. METALLURGICAL LITERATURE CLASSIFICATION                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |  |  |  |  |  |  |  |  |  |  |  |                     |  |  |  |  |  |  |  |  |  |  |  |
| ASME SYMBOLS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |  |  |  |  |  |  |  |  |  |  |  | ASTM SYMBOLS        |  |  |  |  |  |  |  |  |  |  |  |
| TENSILE STRENGTH                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |  |  |  |  |  |  |  |  |  |  |  | COMB. BONDING       |  |  |  |  |  |  |  |  |  |  |  |
| TENSILE STRENGTH                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |  |  |  |  |  |  |  |  |  |  |  | COMB. BONDING       |  |  |  |  |  |  |  |  |  |  |  |

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| <p>CA</p> <p>10</p> <p>Chien y Org. Chem.,<br/>Lomonosov Inst. Fine<br/>Chemical Tech., Moscow.</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |  |
| <p>Synthesis of diaryliodonium salts. K. Kh. Freidman and A. B. Nemovskiy. <i>Compt. rend. acad. sci. U. R. S. S. R.</i>, 607-70 (1940) (in English).—Aromatic organometallic compounds of Sn are the best arylation agents. Reactions with these compounds proceed under mild conditions, often at room temp. in good yields. For example, <math>\text{Ph}_2\text{SnCl}_2</math> reacts with <math>\text{ICl}_3</math> in <math>\text{CH}_2\text{Cl}_2</math> energetically, with liberation of heat, giving a quant. yield of <math>\text{Ph}_2\text{ICl}</math>, thus arylating <math>\text{ICl}_3</math> as well as <math>\text{HgCl}_2</math> according to the equation: <math>\text{ICl}_3 + 2\text{Ph}_2\text{SnCl}_2 \rightarrow \text{Ph}_2\text{ICl} + 2\text{SnCl}_4</math>. To 2 g. (0.016 mol.) <math>\text{ICl}_3</math> in 10 cc. <math>\text{CH}_2\text{Cl}_2</math>, (1:10) <math>\text{HCl}</math> was added 5 g. (0.017 mol.) <math>\text{Ph}_2\text{SnCl}_2</math>. After 0.5 hr. the reaction mixt. was cooled, the ppt. sep'd. and decomp'd. by heating with boiling <math>\text{H}_2\text{O}</math>. After filtration and cooling, 0.5 g. <math>\text{Ph}_2\text{ICl}</math> sep'd. Evapor. of the mother liquor yielded an addnl. 1.15 g. of product, or a total yield of 72%. After reprecipn. from <math>\text{H}_2\text{O}</math> it m. <math>230^\circ</math>, with conversion into a mixt. of <math>\text{Ph}_2\text{ICl}</math> and <math>\text{PhI}</math>. <math>\text{Ph}_2\text{ICl}</math> can be arylated very readily in good yields with <math>\text{PhSnCl}_2</math> at room temp., <math>\text{PhI} + \text{PhSnCl}_2 \rightarrow \text{Ph}_2\text{ICl} + \text{SnCl}_4</math>, under exptl. conditions analogous to those described in the previous synthetic method. The latter method can be used as well for the synthesis of aryl iodochlorides and arsym. iodonium salts of the type <math>\text{RR}_2\text{ICl}</math>. With <math>\text{Ph}_2\text{SnCl}_2</math> and <math>\text{ICl}_3</math>, <math>\text{Ph}_2\text{ICl}</math> and <math>\text{HgCl}_2</math> were obtained. The yield is somewhat lower in the latter reaction, because <math>\text{PhIO}</math> is obtained as a by-product. The product from the latter reaction m. <math>168-170^\circ</math> and is believed to be a double salt in agreement with analysis, <math>\text{Ph}_2\text{ICl} \cdot \text{HgCl}_2</math> (81% yield). This new method of synthesis of iodonium salts has the advantage of simplicity and shortness compared to the methods previously described.</p> <p>W. A. Cook</p> |  |

| 101 AND 102 GROUPS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |  |  |  |  |  |  |  |  |  | PRECIPITATION AND PROPERTIES INDEX |  |  |  |  |  |  |  |  |  | 101 AND 102 GROUPS |  |  |  |  |  |  |  |  |  |
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| <p>60</p> <p>10</p> <p>Mercurioorganic compounds. XVII. Synthesis of mer-<br/>curioorganic compounds of the pyridine series by the diazo<br/>method. A. N. Nesmeyanov and I. F. Lutsenko. <i>J.</i><br/><i>Gen. Chem. (U.S.S.R.)</i> 11:362 3(1941). The following<br/>were synthesized by the diazo method: 3-pyridylmercury<br/>chloride and the corresponding bromide (m. 271.5-<br/>272° (decomp.)) and iodide (m. 270° (decomp.)),<br/>3-pyridylphenylmercury (m. 174-5°) and also bis(5-<br/>benzothio-3-pyridyl)mercury (m. 225-7° (decomp.)).<br/>H. Z. Kamich</p> |  |  |  |  |  |  |  |  |  |                                    |  |  |  |  |  |  |  |  |  |                    |  |  |  |  |  |  |  |  |  |
| <p>ASM-51A METALLURGICAL LITERATURE CLASSIFICATION</p> <p>101 AND 102 GROUPS</p> <p>101 AND 102 GROUPS</p> <p>101 AND 102 GROUPS</p>                                                                                                                                                                                                                                                                                                                                                                                                                                       |  |  |  |  |  |  |  |  |  |                                    |  |  |  |  |  |  |  |  |  |                    |  |  |  |  |  |  |  |  |  |



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| 1ST AND 2ND EDITIONS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |  | 3RD AND 4TH EDITIONS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |  |
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| PROCESSES AND PROPERTIES INDEX                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |  |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |  |
| <p><b>Organic compounds of Hg. XXII. Organometallic Hg compounds of the triphenylmethane series. I. T. Eskin and A. N. Nesmeyanov. Bull. acad. sci. U. R. S. S. Classe sci. chim. 1962, 116-25 (English summary). The authors describe the application of the diazo method of synthesis of Hg-org. compds. of the triphenylmethane series. <math>p\text{-H}_2\text{NC}_6\text{H}_4\text{CHPh}_2</math> (17.5 g.) in 40 cc. concd. HCl and 40 cc. <math>\text{H}_2\text{O}</math> was diazotized by 5 g. <math>\text{NaNO}_2</math> in 15 cc. <math>\text{H}_2\text{O}</math> with addn. of 30 g. ice and keeping the temp. at <math>0^\circ</math>; the filtered soln. was added to a cooled soln. of 25 g. <math>\text{HgCl}_2</math> in 25 cc. concd. HCl, to yield 98.5% <math>(\text{Ph}_2\text{CHC}_6\text{H}_4\text{N}_2\text{Cl}) \cdot \text{H}_2\text{Cl}_2</math>, m. <math>85^\circ</math> (decompr.); the <math>\text{Et}_2\text{O}</math>-<math>\text{EtOH}</math> washings of</b></p> |  | <p>the above contain small amts. of the equimol. double salt. The former (20 g.) is added to 150 cc. <math>\text{Me}_2\text{CO}</math> contg. 5.5 g. <math>\text{HgCl}_2</math>, and with stirring and efficient cooling 7 g. powder. Cu is added to the mixt.; after 20 hrs. the <math>\text{Me}_2\text{CO}</math> is distd. and the residue crystd. from <math>\text{EtOAc}</math>, to yield 80.9% <math>p\text{-H}_2\text{NC}_6\text{H}_4\text{CHPh}_2</math>, m. <math>157-8^\circ</math>. <math>p\text{-H}_2\text{NC}_6\text{H}_4\text{C(OH)Ph}_2</math> (13.75 g.) in 40 cc. <math>\text{H}_2\text{O}</math> and 5 cc. HCl was diazotized with 5 g. <math>\text{NaNO}_2</math> in 15 cc. <math>\text{H}_2\text{O}</math> after addn. of 30 cc. HCl; the filtered soln. was added to 25 g. <math>\text{HgCl}_2</math> in 25 cc. HCl, to yield 91% of the salt <math>(\text{Ph}_2\text{C(OH)C}_6\text{H}_4\text{N}_2\text{Cl}) \cdot \text{H}_2\text{O}</math>, m. <math>81-3^\circ</math> (decompr.); the above (20 g.) stirred into 100 cc. <math>\text{EtOAc}</math> contg. 5.5 g. <math>\text{HgCl}_2</math> was treated with 5 g. Cu powder with cooling and stirring; after 25 hrs., the solvent was distd., the residue washed with petr. ether and extrd. with <math>\text{EtOAc}</math> to yield 46.3% <math>p\text{-Ph}_2\text{C(OH)C}_6\text{H}_4\text{CH}_2\text{Cl} \cdot \text{C}_6\text{H}_5</math> (I), m. <math>157-8^\circ</math> (from benzene); it forms addn. compds. with most solvents; the benzene-fractn. product m. <math>92-3^\circ</math>. <math>e\text{-H}_2\text{NC}_6\text{H}_4\text{CHPh}_2</math> similarly yields <math>e\text{-Ph}_2\text{CHC}_6\text{H}_4\text{H}_2\text{Cl}</math>, m. <math>218-19^\circ</math> (from <math>\text{EtOAc}</math>). <math>e\text{-H}_2\text{NC}_6\text{H}_4\text{C(OH)Ph}_2</math> yields <math>e\text{-Ph}_2\text{C(OH)C}_6\text{H}_4\text{H}_2\text{Cl}</math>, m. <math>163-4^\circ</math> (from <math>\text{Hgrom}</math>). <math>m\text{-Ph}_2\text{CHC}_6\text{H}_4\text{H}_2\text{Cl}</math>, m. <math>145-6^\circ</math> (from <math>\text{EtOAc}</math>), was prepd. by similar diazotization of <math>m\text{-H}_2\text{NC}_6\text{H}_4\text{C(OH)Ph}_2</math>, after treating it in dry <math>\text{Et}_2\text{O}</math> with HCl gas and diazotizing with <math>\text{AcONO}</math>. Dry <math>p\text{-ClH}_2\text{C}_6\text{H}_4\text{CO}_2\text{Et}</math> (35 g.) was added to 72 g. <math>\text{PhMgBr}</math> in 150 cc. <math>\text{Et}_2\text{O}</math>, refluxed for 1 hr. and after the usual decompr., yielded a complex mixt. of organo-Hg compds., from which there was isolated 3.5 g. of product identical with I, m. <math>157-8^\circ</math>; 24.9 g. of <math>\text{PhMg}</math> was also isolated from the <math>\text{Et}_2\text{O}</math> ext. G. M. Kozlovskii</p> |  |
| <p>ASR-CLA METALLURGICAL LITERATURE CLASSIFICATION</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |  |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |  |
| <p>FROM SYNTHESIS</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |  | <p>FROM ANALYSIS</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |  |
| <p>INDEXED BY ONE OR MORE</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |  | <p>INDEXED BY ONE OR MORE</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |  |
| <p>INDEXED BY ONE OR MORE</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |  | <p>INDEXED BY ONE OR MORE</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |  |

[illegible]



| 1ST AND 2ND ORDERS                                                                                                                                                                                                          |  |  |  |  |  |  |  |  |  | 3RD AND 4TH ORDERS |  |  |  |  |  |  |  |  |  |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|--|--|--|--|--|--|--|--|--------------------|--|--|--|--|--|--|--|--|--|
| PROCESSES AND PROPERTIES WORK                                                                                                                                                                                               |  |  |  |  |  |  |  |  |  |                    |  |  |  |  |  |  |  |  |  |
| <div style="display: flex; justify-content: space-between;"> <span>Ca</span> <span>10</span> </div>                                                                                                                         |  |  |  |  |  |  |  |  |  |                    |  |  |  |  |  |  |  |  |  |
| <p>ADDITION of HCl to C<sub>10</sub>H<sub>8</sub> and structure of 2-dimethyl-<br/>indole. A. N. Nemesy and R. K. Finkbein.<br/>Bull. Acad. Sci. U. R. S. S. Chem. Div. 1962, 128-<br/>5. See C. A. 57, 808. G. Borland</p> |  |  |  |  |  |  |  |  |  |                    |  |  |  |  |  |  |  |  |  |
| <p>ACN-56 METALLOGICAL LITERATURE CLASSIFICATION</p>                                                                                                                                                                        |  |  |  |  |  |  |  |  |  |                    |  |  |  |  |  |  |  |  |  |
| LITERATURE                                                                                                                                                                                                                  |  |  |  |  |  |  |  |  |  | LITERATURE         |  |  |  |  |  |  |  |  |  |
| LITERATURE                                                                                                                                                                                                                  |  |  |  |  |  |  |  |  |  | LITERATURE         |  |  |  |  |  |  |  |  |  |



Organic mercury compounds. IX. Heterocyclic addition products of mercuric salts to open-chain dialdehydic compounds. A. N. Nesmeyanov and I. F. Lutsenko. *Bull. acad. sci. U. R. S. S. U. Div. chem. sci.* 1948, 200-204 (English summary); cf. C. A. 47, 3416. Methyl (2 g.) was treated with 16 g.  $\text{Hg}(\text{OAc})_2$  in 50 cc.  $\text{H}_2\text{O}$ ; after 18 hrs. there was added 3.8 g.  $\text{KCl}$  in 20 cc. water to give a quant. yield of 2,5-bis(chloromercurimethyl)-tetrahydrofuran (recrystd. from  $\text{Me}_2\text{CO}$ ), which decomps. on heating without melting. The product treated with 2%  $\text{Na-Hg}$  in water gave 80% several drops 2,5-dimethyltetrahydrofuran as isolated of 1-hexen-3-ol, b.  $130^\circ$ ,  $d_4^{20}$  0.8602; similar reduction in slightly acid soln. (by gradual addn. of 10%  $\text{AcOH}$ ) gave a total of 75% of the above 2 products, with the furan comprising about 25%. To 5.4 g.  $\text{HgCl}_2$  in water was added 0.82 g. in allyl and the pptd.  $\text{Hg}$  compound was filtered off; the filtrate contained 0.7070 g.  $\text{HCl}$  (theoretical, 0.73 g.). 1-Penten-3-ol (4.3 g.) was added to 16 g.  $\text{Hg}(\text{OAc})_2$  in 50 cc. water to yield an oil, which was sol. in alcohol, water; on addn. of a soln. of  $\text{KCl}$  2-(chloromercurimethyl)-tetrahydrofuran pptd. as an oil in 82% yield. Similar reaction with 1-hexen-3-ol gave 80% 2-methyl-5-(chloromercurimethyl)-tetrahydrofuran as an oil; treatment of the reaction mixt. with 2%  $\text{Na-Hg}$  in the presence of sufficient  $\text{AcOH}$  to keep the mixt. slightly acid yielded 2,5-dimethyltetrahydrofuran and 1-hexen-3-ol in combined yield of 80%. Methylamine (5 g.) was added to 30 g.  $\text{Hg}(\text{OAc})_2$  in 100 cc. water; after 12 hrs. the soln. was filtered and treated with  $\text{KCl}$  soln. to yield 26 g. of a solid which dissolved in 10%  $\text{NaOH}$  and on filtration of  $\text{Hg}$  oxides and neutralization gave a white ppt. of 2,5-bis(chloromercurimethyl)morpholine; reduction with  $\text{Na-Hg}$ , as above described, gave 2,5-dimethylmorpholine, b.  $110^\circ$ .

Allyl ether (5 g.) was added to 32 g.  $\text{Hg}(\text{OAc})_2$  in 180 cc. water to yield, after 18 hrs. and addn. of  $\text{KCl}$  soln., 86% of 2,5-bis(chloromercurimethyl)-p-dioxane, m.  $116^\circ$  (from  $\text{EtOH}$ ). Reduction with 2%  $\text{Na-Hg}$  in weakly acid soln. gave the corresponding dioxane, b.  $120^\circ$ ,  $d_4^{20}$  1.4100,  $d_4^{25}$  0.9244. Mercuriated allyl ether (5 g.) was mixed with 5 g. iodine and heated in  $\text{CHCl}_3$  until decolorized to yield 1.1 g. 2,5-bis(iodoethyl)-p-dioxane, m.  $94^\circ$  (from  $\text{EtOH}$ ).  
G. M. Kozlovskii

| 1ST AND 2ND ORDERS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |  |  |  |  |  |  |  |  |  | 3RD AND 4TH ORDERS |  |  |  |  |  |  |  |  |  |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|--|--|--|--|--|--|--|--|--------------------|--|--|--|--|--|--|--|--|--|
| PROCESSES AND PROPERTIES INDEX                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |  |  |  |  |  |  |  |  |  |                    |  |  |  |  |  |  |  |  |  |
| <p><i>Ca</i></p> <p><b>Magnesium-organic compounds. III. Hydronyphenyl-magnesium bromide and its use in the synthesis of other compounds.</b> A. N. Nemytsynov and K. A. Pecherskaya. <i>Bull. acad. sci. U. R. S. S., Classe sci. chim.</i> 1943, 317-18; cf. C. A. 37, 3724<sup>4</sup>.—EtMgBr soln. (contg. 4 g. EtMgBr) was treated with 5 g. <math>\alpha</math>-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>OH to yield an oil, which was washed with Et<sub>2</sub>O, treated with 2.5 g. PbCO and heated on a steam bath for 1 hr.; after treatment with dil. AcOH, extr. with Et<sub>2</sub>O and washing of the latter with dil. NaOH, followed by addn. of 20% NaOH to the washings, gave the Na salt of <math>\alpha</math>-hydronytriphenylcarbinol (28%), which was converted by dil. HCl to the carbinol, m. 140°. The Et<sub>2</sub>O soln. of the original reaction mixt. gave, on evapn., 80% EtMgCl. To 20 cc. of Et<sub>2</sub>O soln. contg. 4 g. EtMgBr was added 5 g. <math>\alpha</math>-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>OH, after which the mixt. was strongly cooled and treated with CO<sub>2</sub> gas for 5 hrs. and decomposed with HCl and extrd. with Et<sub>2</sub>O to yield 20% salicylic acid, m. 155°. Extrn. of the Et<sub>2</sub>O soln. with NaOH gave 0.5 g. PhOH. G. M. K.</p> <p style="text-align: right;">70</p> |  |  |  |  |  |  |  |  |  |                    |  |  |  |  |  |  |  |  |  |
| <p>ASH-51A METALLURGICAL LITERATURE CLASSIFICATION</p> <p>FROM SYMBOLS</p> <p>EXISTING</p> <p>RECENT SYMBOLS</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |  |  |  |  |  |  |  |  |  |                    |  |  |  |  |  |  |  |  |  |

*Pa*

The synthesis of metallo-organic compounds by the method of double displacement salts. XVI. Synthesis of antimony organic compounds. A. N. Kucharsky and K. A. Kochashkov. Dokl. akad. na. U.S.S.R., *Classical chim.*, 1964, 418-81 (English summary); cf. C.A.B., 40844.—When the diammonium salt from  $\text{RC}_6\text{H}_4\text{NH}_2$  is treated with  $\text{SbCl}_5$ , it forms  $\text{RC}_6\text{H}_4\text{N}(\text{CH}_3)_2\text{SbCl}_4$  (I). A suspension of 1.5 moles Zn dust in  $\text{HOAc}$  (300 cc. per 100 g. I) is heated to a temp. 30–35° below the decomposition point of I, usually 70–90°. To this is added 1 mmole I, rapidly with stirring. I decomps. to give varying amounts of  $(\text{RC}_6\text{H}_4)_2\text{SbCl}_4$  (II),  $\text{RC}_6\text{H}_4\text{SbO}$  (III), and  $(\text{C}_6\text{H}_5)_3\text{SbOH}$  isolated as  $(\text{RC}_6\text{H}_4)_2\text{SbOAc}$  (IV), the yields depending on the nature of R. When R is H, the yields are 85% I, 18% II, 64% III, and 16% IV. The total yield using Zn dust is 50%, while if Fe powder is used, the total yield is 65.5%. When R = p-Me, I, m. 104°, gives 21% III and 0.8–4.5% IV. If MeCO is used instead of HOAc, the yields are 18% III, 20% IV, and 30% II. When R = o-Cl, I, decomp. 114°, gives 25% II, m. 185°, 40% III, m. about 114°, and 17% ( $\sigma\text{-ClC}_6\text{H}_4$ )<sub>2</sub>Sb, m. 140°. When R = p-Cl, I, decomp. 111°, gives 10% II, m. 198°, 85% III, m. 115–20°, and 53% IV, m. 130°. When R = m-Cl, I, decomp. 110°, gives 77%  $(\text{CIC}_6\text{H}_4)_2\text{SbCl}_4$ . When R = p-Br, I, decomp. 115°, gives 21% II, m. 198°, 64% III, m. 162–3°, and 15% IV, m. 131–2°. When R = p-t, I, decomp. 108°, gives 28% II, m. 200°, 40% III, m. about 141–5°, and 9% IV, m. 140°. In AcOH at 110–20°.

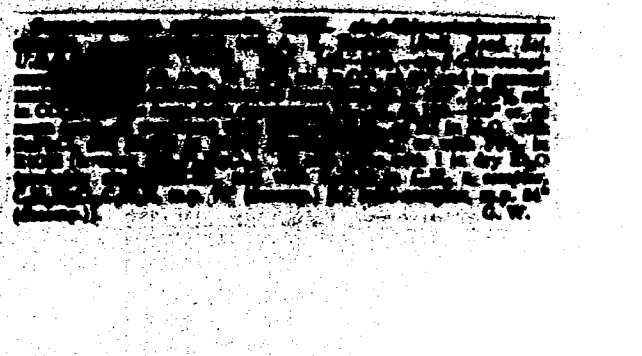
Inst. of Organic Chem., AN SSSR. /  
Chair of Organic Chem., Moscow State U.

the yields are 6.7% II, 38% III, and 30% IV. When R = Clt, I, decomp. 125°, gives mostly  $(\text{HClt})_2\text{Sb}$ . When R = s-MeO, I gives 25% II, m. 245°, and 24.6% III, m. 101°. When R = p-MeO, I, decomp. 131°, gives 9.5% II, m. 180°, 17% III, decomp. 163°, and 8.8% IV. When R = EtO, I gives 40%  $\text{EtOC}_6\text{H}_4\text{SbCl}_4$ , m. 108°. All the double salts with phenols and ethers ppt. as viscous, rather unstable oils which later solidify. When R = NH<sub>2</sub>, I gives 68% III.  
H. M. Leicester

Full trans. in M.

| ASAC-SLA METALLOGICAL LITERATURE CLASSIFICATION |  |  |  |  |  |  |  |  |  | ESOM SYMBOL        |  |  |  |  |  |  |  |  |  |
|-------------------------------------------------|--|--|--|--|--|--|--|--|--|--------------------|--|--|--|--|--|--|--|--|--|
|                                                 |  |  |  |  |  |  |  |  |  |                    |  |  |  |  |  |  |  |  |  |
| ESOM SYMBOL                                     |  |  |  |  |  |  |  |  |  | ESOM SYMBOL        |  |  |  |  |  |  |  |  |  |
| SYMBOL #A                                       |  |  |  |  |  |  |  |  |  | SYMBOL MAY ONE DEC |  |  |  |  |  |  |  |  |  |
| SYMBOL                                          |  |  |  |  |  |  |  |  |  | SYMBOL             |  |  |  |  |  |  |  |  |  |
| SYMBOL                                          |  |  |  |  |  |  |  |  |  | SYMBOL             |  |  |  |  |  |  |  |  |  |

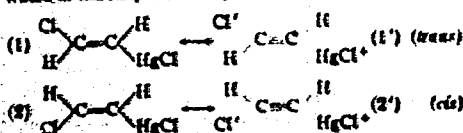


|                                                                                    |  |                           |
|------------------------------------------------------------------------------------|--|---------------------------|
| ALL THE LOW PRESSURE<br><b>PROPERTIES AND PROPERTIES INDEX</b>                     |  | 93                        |
|  |  |                           |
| <b>ASTM-SEA METALLURGICAL LITERATURE CLASSIFICATION</b>                            |  | <b>RESEARCH CENTER</b>    |
| <b>EDSON STEELWORK</b>                                                             |  | <b>EDSON STEELWORK</b>    |
| <b>100000 REF DIV 000</b>                                                          |  | <b>100000 REF DIV 000</b> |
| <b>EDSON STEELWORK</b>                                                             |  | <b>EDSON STEELWORK</b>    |

[illegible]

$\text{HgCl}_2$  has the structure of an organometallic (chlorovinyl)-mercury chloride,  $\text{ClCH:CHHgCl}$ . It is shown that this compound, as obtained by Higuchi by the action of  $\text{C}_2\text{H}_2$  on  $\text{HgCl}_2$  in  $\text{HCl}$  soln., is the trans isomer, and so is the bis(chlorovinyl)mercury, obtained therefrom by Chapman and Jankins (C.A. 18, 3848). The cis isomer of m.p.  $78^\circ$  and greater only, is obtained by addn. of  $\text{C}_2\text{H}_2$  to  $\text{HgCl}_2$  vapor at  $120^\circ$  (Probst, C.A. 37, 3087). With  $\text{ICl}_2$  the compound, *trans*,  $\text{ClCH:CHICl}$  and  $(\text{ClCH:CH})_2\text{ICl}$ , *trans*, plus  $\text{HgCl}_2$ ; the same chlorovinyl and bis(chlorovinyl) iodochlorides can be synthesized by direct chlorination of  $\text{ClCH:CHI}$  or by direct addn. of  $\text{ICl}_2$  to  $\text{C}_2\text{H}_2$ ; they are consequently, in this respect, true organometallic compounds. Beta. of  $\text{SbCl}_3$  with  $\text{C}_2\text{H}_2$  at  $180^\circ$  and distn. at  $165-70^\circ$  at 3 mm. gives 2 cryst. compds. which can be sepd. by recrystn. into 80% of a higher-melting ( $93-94^\circ$ ) and less-sol.  $(\text{C}_2\text{H}_3)_2\text{SbCl}_2$ , and about 4% is an isomer m.  $61-2^\circ$ . The former is considered to be the *trans*, the latter the *cis* form of tris(chlorovinyl)antimony dichloride. Reduction gives the 2 corresponding tris(chlorovinyl)stibines:  $(\text{ClCH:CH})_3\text{Sb}$ ; *trans*-, m.  $48-9^\circ$ , and *cis*-, b.  $131-2^\circ$ . For details of prepn., data, and reactions, see the following abstract. With  $\text{HgCl}_2$ , the two  $(\text{ClCH:CH})_2\text{SbCl}_2$  and the two  $(\text{ClCH:CH})_3\text{Sb}$  quantitatively exchange  $\text{SbCl}_2$  for  $\text{HgCl}_2$  without change of configuration to give  $\text{ClCH:CHHgCl}$ . There is complete analogy between these compds. and the corresponding Hg compds. with  $\text{C}_2\text{H}_2$ . The Hg and Sb compds. described behave largely as organometallic compds. but on the other hand

trated in the simplest case by



The assumption is corroborated by the absence in the Raman spectrum of *trans*-bis(chlorovinyl)mercury, of double- and of triple-bond frequencies and the presence of an intermediate frequency  $1770\text{ cm}^{-1}$ ; a dipole moment for the *trans*- $\text{ClCH:CHHgCl}$  of 1.64 instead of the calcd. 1.34 which would correspond to structure (1), and of 2.75 for the *cis* form instead of the 4.03 calcd. for structure (2). This would mean that in the *trans* form (1') is present in the amt. of 14% and that in the *cis* structure (2') amounts to 30%. The primed structures account for the dissoci. with elimination of  $\text{C}_2\text{H}_2$ , while the left-hand formulas represent the organometallic behavior. Extension of this point of view leads to assuming the same type of resonance in addn. compds. of metal salts and olefinic hydrocarbons such as  $\text{HOCH}_2\text{CH}_2\text{HgCl}$ ,  $\text{EtOCH}_2\text{CH}_2\text{HgCl}$ ,  $\text{AcOCH}_2\text{CH}_2\text{HgOAc}$ ,  $\text{C}_6\text{H}_5\text{NCH}_2\text{CH}_2\text{HgCl}$ , etc. Analogous resonance relations might prevail in many other cases such as hydrides of boron, aluminum, etc., Adams and Volwiler (C.A. 18, 122) addn. products of chloro anhydrides and aldehydes, including the case of diphosgene. The basic idea is related to Pauling's formula (Nature of the Chemical Bond, C.A. 33, 6700) of diborane and Goria, Walter, and Ryring's resonance representation of the ethane mol. (C.A. 33, 7-8).

Organic compounds of antimony. II. Synthesis and structure of the products of addition of antimony pentachloride to acetylene. A. N. Nemeyanov and A. B. Barinov (Inst. Org. Chem., Acad. Sci. U.S.S.R.). *Bull. Acad. Sci. U.S.S.R., Chem. Sci. Div.* 1948, 261-60 (English summary); cf. C.A. 40, 6230<sup>2</sup>.—The prep. of *trans*-(*trans*-chlorovinyl)antimony dichloride, mentioned in the foregoing abstract, is described in detail. Acetylene gas is absorbed in a soln. of  $SbCl_5$  in 80% alkali, with some  $HgCl_2$  added; the mixt. is maintained at 80-100° for 3-4 hrs., then at 150-75° until the absorption is ended. The fraction b.p. 180-5° (or b.p. 165-70°), corresponding to a yield of 80%, plus the petr. ether ext. of the lower fraction (addnl. 8-10%), is recrystd. from 90% alc., yielding a compd. m. 68-4°,  $d_4^{20}$  1.7638,  $\gamma_D^{20}$  36.88 dyne/cm. From the mother liquor, petr. ether exts. (yield 2-4%) an isomeric compd., m. 61-2°, easily sol. in all org. solvents,  $d_4^{20}$  1.7638,  $\gamma_D^{20}$  37.40 dyne/cm. Of the 4 possible isomers, only these 2 could be isolated. Tentatively, the higher-melting isomer is considered to be the *trans-trans-trans*, the lower-melting the *cis-cis-cis* form. With iodine and with  $Br_2$ , the 2 isomers react, forming, resp.,  $CICH:CHI$  and  $CICH:CHI$ , and eliminating  $SbCl_5$  and  $SbCl_3$ , resp. Reduction to the corresponding *trans*-(*trans*-chlorovinyl)antimony trichloride is effected easily with  $NaBH_4$  in wateralc. soln. The *trans* compd. m. 64-4°, b.p. 121°, b.p. 168°,  $d_4^{20}$  1.7021,  $\gamma_D^{20}$  36.10. The *cis* form is a colorless liquid, b.p. 121-2°, b.p. 134°,  $d_4^{20}$  1.6070,  $d_4^{20}$  1.7181,  $\gamma_D^{20}$  36.93.

*Bis*-(*trans*-chlorovinyl)antimony trichloride, prepd. by the action of  $C_2H_2$  on  $SbCl_5$ , the temp. being maintained at not higher than 60° (yield 70-80%), colorless crystals, m. 61-2°, hygroscopic, immediately hydrolyzed in water, and without decompos. in dil. HCl, decompos. by acid alkali and on heating in alc. by thionine and benzyl alcohol, with evolution of  $C_2H_2$ . With  $SO_2$ , it forms the *bis*-(*trans*-chlorovinyl)sulfone, liquid, b.p. 68°, b.p. 98°,  $d_4^{20}$  1.4012,  $n_D^{20}$  1.4070. Reaction of  $(CICH:CHI)_3SbCl_5$  with metallic Sb in ether and subsequent vacuum distn. permits the isolation of 2 organometallic compds. of trivalent Sb, viz., *bis*-(*trans*-chlorovinyl)antimony chloride [*bis*-(*trans*-chlorovinyl)chlorostibine], thick colorless liquid, b.p. 113-18°, and (*trans*-chlorovinyl)antimony dichloride [(*trans*-chlorovinyl)dichlorostibine], colorless liquid, b.p. 103-5°,  $d_4^{20}$  2.1488. Pyrolysis of *trans*-( $CICH:CHI$ ) $SbCl_5$  at 800-900° yields  $C_2H_2$ ,  $CICH:CHI$ ,  $CICH:CHCH:CHCl$ , and  $H_2Cl$ .  $AgNO_3$  pptn., along with the complex  $[(CICH:CHI)_3Sb]AgNO_3$ , the acetylide  $AgC:CAgAgNO_3$ . Structural considerations involving the assumption of resonance are given in the foregoing abstract. N. Thon

A.S.C. S.L.A. METALLURGICAL LITERATURE CLASSIFICATION

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| SYNOPSIS AND PROPERTIES INDEX                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                   |
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| <p>Synthesis of organometallic compounds by the use of double diazonium salts. XVII. Tetraphenyllead. A. N. Neumayr and K. A. Kochshkov. <i>Bull. Acad. Sci. U.S.S.R., Class. Chem.</i> 1948, 522-4; <i>cf. C.A.B.</i> 43, 4320. Addn. of Pb to <math>\text{PhN}_2\text{BF}_4</math> in <math>\text{C}_6\text{H}_6</math> at 0° yields <math>\text{PbPh}_4</math> (15%), m. 236°. In <math>\text{EtOH}</math>, evolution of <math>\text{N}_2</math> is observed only at 35°, but no <math>\text{PbPh}_4</math> is obtained. The reaction mechanism is discussed. XVIII. Tris (<i>p</i>-sulfonylphenyl) bismuth. <i>Ibid.</i> 524-6. (p-<math>\text{Nf}_3\text{SO}_2\text{C}_6\text{H}_4\text{N}_2\text{CH}_3</math>, <math>\text{HCl}</math>, (Chalkley, <i>C.A.B.</i> 35, 3623) with 50% excess of <math>\text{Bi}</math> in <math>\text{C}_6\text{H}_6</math>, at 30°, or <math>\text{EtOH}</math> at 150°, affords, resp., 25 or 6% of tris (<i>p</i>-sulfonylphenyl)bismuth (I), m. 213°. With <math>\text{Bi}</math> in <math>\text{CCl}_4</math>, I gives p-<math>\text{ClC}_6\text{H}_4\text{SO}_2\text{Nf}_3</math> in nearly theoretical yield. Treatment of the double salt with <math>\text{Cu}</math> in <math>\text{C}_6\text{H}_6</math>, or <math>\text{EtOH}</math> affords mainly p-<math>\text{ClC}_6\text{H}_4\text{SO}_2\text{Nf}_3</math>. H. A.</p> |                                                   |
| <p>1. METALLURGICAL LITERATURE CLASSIFICATION</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                                   |
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| 1ST AND 2ND OPD'S                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |  | PROCESS AND PROPERTY INDEX |  | 100 AND 2TH EQUIS |  |
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| <p>Organometallic compounds of mercury. XXXII. (I).<br/>           The preservation of the geometrical configuration of the<br/>           chlorovinyl group in thermal decomposition reactions. A.<br/>           M. Krasnoperov, A. E. Borisyuk and A. N. Ozerkov<br/>           (Inst. Org. Chem., Acad. Sci. USSR, Bull. Acad.<br/>           Sci. USSR, Div. Chem. Sci., 1968, 100-101 in English<br/>           048); <i>ibid.</i> 1968, 100-101. <i>trans</i>-(ClCH:CH)Sb (II)<br/>           and HgCl<sub>2</sub> heated in Me<sub>2</sub>CO give 80.5% <i>trans</i>-ClCH:CH:<br/>           HgCl (III), m. 122° (decomp.). Similarly, <i>cis</i>-(ClCH:<br/>           Cl)Sb (III) and HgCl<sub>2</sub> in abs. EtOH give 96% <i>cis</i>-(<i>Z</i>-<br/> <i>chlorovinyl</i>)mercuric chloride (IV), m. 78.5-8°. In neither<br/>           reaction is the other isomer formed, but when a mixt. of I<br/>           and II reacts with Me<sub>2</sub>CO, a mixt. of II and IV results.<br/>           When IV is treated with H<sub>2</sub> in dry C<sub>6</sub>H<sub>6</sub> it gives 70.8%<br/> <i>cis</i>-<i>3,4</i>-(<i>Z</i>-chlorovinyl)mercury (V), which does not solidify<br/>           in solid CO<sub>2</sub>, d<sub>4</sub><sup>20</sup> 2.8000, n<sub>D</sub><sup>20</sup> 1.8308, <i>AR</i> found 40.03,<br/> <i>calcd.</i> 40.03 (molecular formula) 46.66 g/mole, parachor calcd.<br/>           340.3, found 340.9. When V is heated at 100-5° or treated<br/>           with KCN, Na<sub>2</sub>CO<sub>3</sub>, KI, or P<sub>2</sub>H<sub>4</sub>, it decomps. to HgCl<sub>2</sub> and<br/>           C<sub>2</sub>H<sub>4</sub>. It is thus a quasicomplex compd. V and HgCl<sub>2</sub> in<br/>           dry Et<sub>2</sub>O give 96% IV. Similarly, V and HgBr<sub>2</sub> give 97.4%<br/> <i>cis</i>-(<i>Z</i>-chlorovinyl)mercuric bromide, m. 101-2° (decomp.).<br/>           Cl and <i>trans</i>-(ClCH:CH)Hg in CCl<sub>4</sub> give II. V and Cl<br/>           form IV. Cl reacts with I at 120-30° to give <i>trans</i>-ClCH:<br/>           CHCl. In all these reactions the stereochem. configura-<br/>           tion of the chlorovinyl group remains unchanged as it is<br/>           transferred from atom to atom. H. M. Leicester</p> |  |                            |  |                   |  |
| <p>ASAC-ELA METALLURGICAL LITERATURE CLASSIFICATION</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |  |                            |  |                   |  |
| SOURCE SYNOPTIC                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |  | SOURCE NUMBER              |  | SOURCE DATE       |  |
| LITERATURE                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |  | LITERATURE                 |  | LITERATURE        |  |

| 1ST AND 2ND COPIES                                                                                                                                                                                                                                                                                                                                                                                                                                        |  |  |  |  |  |  |  |  |  | 3RD AND 4TH COPIES        |  |  |  |  |  |  |  |  |  |
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| PROCEDURES AND PROPERTIES INDEX                                                                                                                                                                                                                                                                                                                                                                                                                           |  |  |  |  |  |  |  |  |  |                           |  |  |  |  |  |  |  |  |  |
| <p><i>ca</i></p> <p>Organic compounds and the periodic system. A. N. Nesmeyanov. <i>Soviet Chem.</i> 14, 221-22 (1945). The structure and reactions of org. compds. of those elements (both metallic and non-metallic) that are most commonly found in inorg. compds., e.g., Hg, Sn, As, Te, W, Bi, are reviewed, with SI references. The importance of their intermediate position between inorg. and org. chemistry is pointed out. H. M. Leicester</p> |  |  |  |  |  |  |  |  |  |                           |  |  |  |  |  |  |  |  |  |
| <p>10</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                 |  |  |  |  |  |  |  |  |  |                           |  |  |  |  |  |  |  |  |  |
| <p>ASR-55A METALLURGICAL LITERATURE CLASSIFICATION</p>                                                                                                                                                                                                                                                                                                                                                                                                    |  |  |  |  |  |  |  |  |  |                           |  |  |  |  |  |  |  |  |  |
| <p>1ST AND 2ND COPIES</p>                                                                                                                                                                                                                                                                                                                                                                                                                                 |  |  |  |  |  |  |  |  |  | <p>3RD AND 4TH COPIES</p> |  |  |  |  |  |  |  |  |  |
| <p>1ST AND 2ND COPIES</p>                                                                                                                                                                                                                                                                                                                                                                                                                                 |  |  |  |  |  |  |  |  |  | <p>3RD AND 4TH COPIES</p> |  |  |  |  |  |  |  |  |  |

**CIA-RDP86-00513R0011366200**

10

PROCESSING AND PRESERVATION

117 AND 120 CODES

WESEMEYANOV, R. N.

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Organomercury compounds. **XVIII.** Synthesis of two stereoisomeric chlorides of bis(2-chlorovinyl)tin starting with stereoisomers of bis(2-chlorovinyl)mercury. A. N. Nemesyayov, A. E. Borisov, and R. N. Abramova. *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk* 1946, 647-50; cf. C.A. 42, 5846g. — From 2 g. *trans*-(ClCH:CH)<sub>2</sub>Hg in 5 ml. abs. EtOH slightly acidified by HCl and 1.2 g. dry SnCl<sub>4</sub> in 5 ml. abs. EtOH, heated 10 min. at 45-50°, then let stand 1 hr., was isolated 97% *trans*-(ClCH:CH)<sub>2</sub>SnCl<sub>2</sub>, m. 77.5-8.5° (from petr. ether), which loses C<sub>6</sub>H<sub>6</sub> with 15% KOH, while HgCl<sub>2</sub> in EtOH gives the solid *trans*-(ClCH:CH)<sub>2</sub>Hg, decomp. 123°. Similar reaction of SnCl<sub>4</sub> with the *cis-cis* isomer after 7 hrs. at 65-70° gave 100% Hg and the *cis-cis* isomer of (ClCH:CH)<sub>2</sub>SnCl<sub>2</sub>, m. 100-2°, s' 1.5675, d' 1.7494, which loses C<sub>6</sub>H<sub>6</sub> only with 60% KOH, while heating 2 hrs. in alc. with HgCl<sub>2</sub> gave 84% *cis-cis*-(ClCH:CH)<sub>2</sub>HgCl<sub>2</sub>, m. 77-8° (from petr. ether). G. M. K.

450.62 METALLURGICAL LITERATURE CLASSIFICATION

FROM SOURCE

INTERNAL NO.

EXTERNAL NO.

DATE

REMARKS

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100

*Nesmeyanov, A. N.*

KOSHTOYANTS, Kh. S.; VAVILOV, S. I.; VOLGIN, V. P.; BRUYEVICH, N. G.; ZAVARITSKIY, A. N.;  
NESMEYANOV, A. N.; SEGAL, B. I.

Ed.: Anniversary Collection, Devoted to the 30th Year of the Great October Socialist  
Revolution. In two parts.

M.-L., AN SSSR, 1947. Part 1, 712 s.; part 2, 835 s.

NESMEYANOV, A. N.

PA 872

- USSR/Chemistry-Onium Compounds  
Organic compounds, synthesis  
Organic compounds, decomposition

Feb 1947

"Decomposition and Formation of Onium Salts and  
Synthesis of Organo-elemental Compounds through  
Onium Compounds," A. N. Nesmeyanov, L. G.  
Makarova, 6 pp

"Izv Ak Nauk Khim" No 2

Decomposition of diazonium fluoroborate in the  
medium of the benzene derivative, containing meta  
directing substituents, to further study on the  
decomposition of diphenyl-iodonium salts.

872



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10

Organomercury compounds. XXXIV. Synthesis of  
halomercapturic aldehydes and halomercapturic acids. A.  
N. Nemyaynov, I. P. Entenko, and M. I. Vereshchagin.  
Dokl. akad. na. S.S.S.R., Classe de chim. 1947, 63 9

(in Russian); cf. C.A. 40, 4659P. To a filtered soln. of 32 g.  $\text{Hg}(\text{OAc})_2$  in 150 cc. water was added with shaking 10 g.  $\text{C}_6\text{H}_5\text{Cl}_3\text{ClO}_4$ ; the soln. after removal of  $\text{Hg}$  by filtration was treated with 7.5 g.  $\text{KCl}$  in the min. amt. of  $\text{H}_2\text{O}$  to give 86%  $\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{Cl}_3\text{ClO}_4$  m. 130-1° (from hot water); if  $\text{KCl}$  is used in the pptn., one obtains 85%  $\text{BzC}_6\text{H}_4\text{C}_6\text{H}_4\text{Cl}_3\text{ClO}_4$  m. 128-9° (from water). If  $\text{C}_6\text{H}_5\text{Cl}_3\text{ClO}_4$  (no-Ar) is used (instead of the  $\text{Hg}$  deriv.), the yield drops to 38%;  $\text{BzC}_6\text{H}_4\text{C}_6\text{H}_4\text{Cl}_3\text{ClO}_4$  gives an 80% yield, while  $\text{C}_6\text{H}_5\text{Cl}_3\text{ClO}_4$  gives 85%.  $\text{C}_6\text{H}_5\text{Cl}_3\text{ClO}_4$  (20 g.) in 100 cc.  $\text{CCl}_4$ , slowly treated with 32 g.  $\text{Be}$  in  $\text{CCl}_4$ , gave 80%  $\text{dibromochloro Be}$  rather, the 102-3° (this 78 g.), added to  $\text{MeMgBr}$  from 2.5 g.  $\text{Mg}$ , treated 1 hr., allowed to stand overnight, and decomposed by dil.  $\text{HCl}$ , gave 82% 2-bromo-2-butylpyrene, the 73-4°;  $\text{C}_6\text{H}_5\text{Cl}_3\text{ClO}_4$  1.1432, d<sub>4</sub> 1.1434; (this 23 g.) and 30 g. powdered  $\text{KOH}$  treated to 240-50° gave 68% isopropenyl fluorene, b. 112.5-13°; n<sub>D</sub> 1.4100, d<sub>4</sub> 1.2700; (this 1.2 g.) was added to 2.2 g.  $\text{Hg}(\text{OAc})_2$  in 16 cc. water and, when the mild reaction ceased, the mixt. was filtered and the filtrate treated with 0.75 g.  $\text{KCl}$  to give 88%  $\text{AcCH}_2\text{C}_6\text{H}_4\text{Cl}_3\text{ClO}_4$  m. 114° (from  $\text{MeOH}$ ).  $\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{Cl}_3\text{ClO}_4$  (7 g.) and 12 cc. of (iso- $\text{PrO})_2\text{Al}$  soln. (no concn. given) were allowed

to stand 3 days, treated with 10% NaOH until the solids dissolved, then with  $\text{C}_6\text{H}_6$ , to give  $\text{HgCl}_2\text{C}_2\text{H}_3\text{Cl}_2$ , m. 181° (from MeOH), which evolves  $\text{Cl}_2$  on treatment with HCl.  $\text{HgCl}_2\text{C}_2\text{H}_3\text{Cl}_2$  with Be in  $\text{CHCl}_3$  gave  $\text{BeHgCl}_4$ , which rapidly polymerizes to a white solid. Condensation of  $\text{Hg}(\text{Me})_2$  with  $\text{Cl}_2$ ,  $\text{CHCl}_3$  in  $\text{EtOH}$ , followed by addn. of  $\text{KCl}$ , also gives  $\text{ClHgCl}_2\text{C}_2\text{H}_3\text{Cl}_2$ . XXX. Reaction of acetylene and mercuric chloride in the absence of a solvent. R. Kh. Froelkina and O. V. Nogina. *Ibid.* 105-6. —  $\text{HgCl}_2$  (3 g.) dispersed with glass wool was treated with a stream of  $\text{C}_2\text{H}_2$  3 hrs. at 60 mm. and the product extrd. with  $\text{CCl}_4$  and  $\text{CCl}_2$ , condng. gave 2.15 g. *trans*-2-chlorovinylmercury chloride, m. 76-7°, which with  $\text{NH}_4\text{OH}$  gave *trans*-2-chlorovinylmercury (liquid). The product can be crystd. from  $\text{EtOH}$ , pet. ether, or  $\text{EtOH}$ . Examn. of the product with a petrographic microscope reveals only traces of *trans*-2-chlorovinylmercury chloride. If the  $\text{Cl}_2$  contains a trace of moisture, the same procedure gives *trans*-2-chlorovinylmercury chloride, m. 46-48°, which after repeated crystn. (from an unspecified solvent), m. 123-4° (decompos.). G. M. Kozlovski

| 1ST AND 2ND DEGREE                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |  | PROCESSING AND PREPARATION |  | 3RD AND 4TH DEGREE |  |
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| CA                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |  | 10                         |  |                    |  |
| <p>Decomposition and formation of osmium salts and synthesis of heteroorganic compounds through osmium compounds. II. Two types of decomposition of osmium salts. A. N. Neameyannov and I. G. Makarova. <i>Bull. Acad. sci. U.R.S.S., Classe sci. chim.</i> 1947, 213-18 (in Russian); <i>J. C.A.</i> 40, 4697. — The 2 types of osmium compd. decomposn. discussed in Part I, i.e. transfer of either a Ph free radical or a Ph cation, were investigated in the diazonium series, using <math>\text{PhNO}_2</math> as solvent, which gave <math>m\text{-PhC}_6\text{H}_4\text{CO}_2\text{Et}</math>, <math>\text{NO}_2\text{C}_6\text{H}_4\text{Ph}</math>, and in <math>\text{EtO}_2\text{B}</math>, which gave <math>m\text{-PhC}_6\text{H}_4\text{CO}_2\text{Et}</math>. It is concluded that benzenediazonium borofluoride (I) on decomposn. transfers its Ph radical as a Ph cation. I (84.5 g.) was gradually added to 230 g. <math>\text{PhNO}_2</math> at <math>70^\circ</math> over 2.5 hrs. and stirred 3.5 hrs. at <math>70-80^\circ</math>, giving: 11% <math>\text{PhF}</math>, b. <math>88-4^\circ</math>, n<sub>D</sub><sup>20</sup> 1.4088, and 5 g. <math>m\text{-NO}_2\text{C}_6\text{H}_4\text{Ph}</math>, b. <math>140-6^\circ</math>, m. <math>86^\circ</math> (from petr. ether, after sublimation). To 300 g. <math>\text{EtO}_2\text{B}</math>, at <math>100-10^\circ</math>, there was added over 2.5 hrs. 96 g. I and the mixt. was stirred 2 hrs. at <math>100^\circ</math>, giving 12.2% <math>\text{PhF}</math> and 9.96 g. <math>\text{PhOEt}</math> mixed with <math>m\text{-NO}_2\text{C}_6\text{H}_4\text{Ph}</math>; the latter was a liquid which was filtered from the solid <math>\text{PhOEt}</math>, the crude yield being 4.2 g.; on hydrolysis by hot <math>30^\circ</math> <math>\text{NaOH}</math> it gave <math>m\text{-PhC}_6\text{H}_4\text{CO}_2\text{Et}</math>, m. <math>150^\circ</math>. Phenyltrimethylammonium borofluoride, <math>\text{C}_6\text{H}_5\text{N}^+\text{Me}_3\text{B}^-\text{F}_4</math>, prep'd. by mixing aq. solns. of <math>\text{PhMe}_3\text{NOH}</math> and <math>\text{NaBF}_4</math>, treated at <math>140-80^\circ</math> with 72 g. I over 3.5 hrs. was melted, treated at <math>175^\circ</math> with resulting distn. and the mixt. stirred 15 min. at <math>175^\circ</math>, with resulting distn. of 7 g. <math>\text{PhF}</math>; the main mass, treated with 40% <math>\text{KOH}</math>, filtered, comd., and ext'd. with <math>\text{Et}_2\text{O}</math>, gave a little <math>\text{PhNO}_2</math>, m. <math>127^\circ</math> g. <math>m\text{-Me}_2\text{NC}_6\text{H}_4\text{Ph}</math>, b. <math>171-3^\circ</math> (picole, m. <math>167^\circ</math>), and 0.45 g. <math>p\text{-Me}_2\text{NC}_6\text{H}_4\text{Ph}</math>, m. <math>126^\circ</math> g. m. Kozoloff</p> |  |                            |  |                    |  |
| ASO-SLA METALLURGICAL LITERATURE CLASSIFICATION                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |  |                            |  |                    |  |
| FROM SYNONYMS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |  |                            |  |                    |  |
| SYNONYMS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |  |                            |  |                    |  |
| ALLEGATIONS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |  |                            |  |                    |  |
| ALLEGATIONS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |  |                            |  |                    |  |

NESMEYANOV, A.N.

CA

Organomercury compounds. XXXVI. Rearrangement of stereoisomeric metal organic compounds of the ethylenic series on illumination with ultraviolet radiation. A. N. Nesmeyanov, A. F. Borisov, and A. N. Abramova. (Inst. Org. Chem. Acad. Sci. U.S.S.R., Moscow). Bull. Acad. Sci. U.R.S.S., Classe sci. chim. 1947, 289-93 (in Russian); cf. C.A. 42, 4148i. — Fused *trans-trans*-(CHCl:CH)<sub>2</sub>Hg (I), m. 71°, exposed 17 hrs. to a quartz Hg-vapor lamp at a distance of 2-3 cm., gave 45% liquid *cis-cis*-(CHCl:CH)<sub>2</sub>Hg (II), b. 52.5-3° under  $1.3 \times 10^{-3}$  mm. Hg,  $d_4^{20}$  2.7929,  $n_D^{20}$  1.6124,  $\epsilon$  47.18 dynes/cm.; these consts. are better than those previously given for a less pure product. The yield increases with the length of exposure, e.g., 10, 42, and 76 hrs., 24, 47, and 65.5%. With HgCl<sub>2</sub>, II gave quantitatively *cis*-(CHCl:CH)-HgCl (III), m. 78-8.5°; the same product was obtained in the reaction between HgCl<sub>2</sub> and II exposed 12 hrs. to ultraviolet light; the total absence of *trans*-(CHCl:CH)-HgCl (IV), m. 124°, indicates that the photochem. rearrangement of I gives no *cis-trans* isomer. The photochem. rearrangement of I into II is not reversible. While IV in the fused state is unaffected by ultraviolet light, in C<sub>6</sub>H<sub>6</sub> (4 g. in 25 ml.) 50 hrs. exposure at a distance of 2-3 cm. gave 23.7% III; in abs. alc. and in PhMe, the yields are lower (10 and 8%, resp.). N. Thon

chem 9

NESMEYANOV, A. N.

PA 15T22

USSR/Chemistry - Mercury  
Chemistry - Isomers

May/Jun 1947

"Organometallic Compounds of Mercury: XXXVI, The  
Rearrangement of Stereoisomeric Organometallic  
Compounds of the Ethylene Series by Illumination  
with Ultraviolet Rays," A. N. Nesmeyanov, A. E.  
Borissov, A. N. Abramova, 4 pp

"Izv Ak Nauk Otd Khim Nauk" No 3

Rearrangement of mercury di(trans-beta-chlorovinyl)  
to liquid mercury di(cis-beta-chlorovinyl) by il-  
lumination with quartz mercury lamp ultraviolet rays.

15T22

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| 1ST AND 2ND COPIES                          |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | AND 4TH COPIES |  |
| CA                                          | <p>Organomercury compounds. XXXIX. Reaction of 2-chlorovinyl compounds of mercury with bases. A. N. Neumeyanov, A. Kochetkov, and K. Kh. Prekhlina. <i>Dokl. Akad. Sci. U.R.S.S., Class. Sci. Chem.</i> 1947, 667-9 (in Russian); cf. C.A. 42, 1371g. — In the previous papers instances were given in which complete elimination of <math>\text{C}_2\text{H}_2</math> from 2-chlorovinyl metallodg. compds. was observed on reaction with substances capable of binding the halogen residue. A new reaction type is now reported in which adducts of <math>\text{HgCl}_2</math> and <math>\text{C}_2\text{H}_2</math> are treated with nucleophilic reagents which lead to the loss of <math>\text{HCl}</math> and give explosive <math>\text{Hg}</math> acetylides. Thus, quant. loss of <math>\text{HCl}</math> takes place when bis(<i>trans</i>-2-chlorovinyl)mercury (I) is treated in dry <math>\text{EtOH}</math> or <math>\text{Et}_2\text{O}</math> with <math>\text{EtONa}</math>, <math>\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2</math>, piperidine, <math>\text{NaOAc}</math>, <math>\text{K}</math> phthalimide, <math>\text{Na}</math> phenylacetylide, or <math>\text{AgNO}_3</math>. Titration of I with 5% <math>\text{NaOH}</math> leads to slow pptn. of <math>\text{Hg}</math> acetylide. Analysis of some of the acetylides obtained above gave the av. compn. <math>\text{C}_4\text{H}_4\text{HgCl}</math>, indicative of partial loss of <math>\text{C}_2\text{H}_2</math>. Treatment of the acetylides with <math>\text{HCl}</math> leads to substantial loss of <math>\text{C}_2\text{H}_2</math>, which is unprecedented in other classes of 2-chlorovinyl compounds. The structure of the compounds discussed here may be represented by the resonance of <math>\text{ClCH}:\text{CHHgCl} \longleftrightarrow \text{Cl}^-\text{CH}^+\text{CHHgCl} \longleftrightarrow \text{Cl}^-\text{CH}:\text{CH}^+\text{CHHgCl}</math>. The easy loss of <math>\text{HCl}</math> in these metallodg. derivs. is explainable on the basis of a structure best shown as: <math>\text{Cl}-\text{CH}:\text{C}(\text{H})-\text{HgCl}</math>, where (the compound behaves like a quasi-complex compound because of hyperconjugation, which might be termed <math>\alpha</math>-hyperconjugation, as contrasted to the usual <math>\pi</math>-hyperconjugation. The determining factor is the considerable wt. of the ionic structure in the C-Hg bond. (No anal. data are given in the paper.)</p> |                |  |
|                                             | <p>10</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                |  |
| <p>ALB-514 METALLURGICAL LITERATURE CLA</p> |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                |  |
| <p>RECEIVED JUL 21 1947</p>                 |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                |  |
| <p>RECEIVED JUL 21 1947</p>                 |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                |  |

NESMAYANOV, A. N.

USSR/Acad Sci  
Chem - Acad Sci  
Radium

Aug 1947

"June Session of Department of Chemical Sciences" 1½ pp

"Vest Akad Nauk SSSR" No 8

Session called in honor of 25<sup>th</sup> anniversary of the Radium Institute of the Academy of Sciences. I. Ye. Starik, Acting Director of the Radium Institute, read a paper on the work of the Institute. Twenty-eight workers awarded prizes and medals: Academician V. G. Khlopin, Director of the Institute; Academician P. I. Lukirskiy; B. A. Nikitin, I. Ye. Starik, and A. A. Grinberg, Corresponding Members of the Academy of Sciences; M. G. Meshcheruakov, M. A. Pasvik-Khlopina, and A. Kh. Ratner, Candidates in Chemical Sciences, etc. Several scientists, among them A.N. Nesmayanov and A. F. Kapustinskiy, submitted articles and papers for judgment.

PA 57T9

NESMEYANOV, A. N.

USSR/Chemistry - History  
Chemistry - Biographies

Sep/Oct 1947

"Soviet Chemistry on Eve of Thirtieth Anniversary of October Revolution," A. A. Balandin,  
B. M. Berkengeym, A. N. Nesmeyanov, Moscow, 20 pp

"Uspekhi Khimii" Vol XVI, No 5

General historical article briefly recounts more important works of Soviet scientists,  
such as Lomonosov, Gess, Bakh, Vernadskiy, Fersman, etc. Pictures of the more  
important of these scientists.

PA40T8

NESMEYANOV, A. N.

USSR/Chemistry - Sulfuration  
Chemistry - Solution

Jan 1947

"Sulfuration of Pyrrole," A. P. Teren't'yev, M. A. Shadkhina 3 pp

"Dok Ak Nauk SSSR" Vol LV, No 3

Submitted by A. N. Nesmeyanov, Moscow State University imeni M. V. Lomonosov, 31 May 46.  
This process discovered by Chiamichian and Zil'ber in 1885. Later experiments by  
Teren't'yev and Shadkhina. Behavior of pyro-sulphuric acid during reaction shows a  
great increase in the sulphur group, and this is also characteristic for the  
d-substituted pyroles.

FA 21T8



NESMEYANOV, A. N. Academician

Discovery of Buyouny-Mashtagi Oil Deposits

Soviet Source: N. Trud #132, 7 June 47, Moscow

Abstracted in USAF "Treasure Island" Report No. 47548, on file in  
Library of Congress, Air Information Division

NESMEYANOV, A. N.

PA 66T27

USSR/Chemistry - Organic Compounds  
Chemistry - Lead Compounds

Jan/Feb 1948

"Quasi-Complex Lead Compounds," A. N. Nesmeyanov,  
P. Kh. Freydlina, A. Kochetov, Inst of Org Chem, Acad  
Sci USSR, 7 pp

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 1

Describes how lead organic compounds belonging to the  
/ -vinyl chloride group are obtained. Gives details  
of research on the interaction of these compounds  
with mercury and chloride of tin, and on their reac-  
tion to the action of alkalis, water, Grignard re-  
agent, and hydrazidine.

222

66T27

CA

Potassium fluoride as an ending of alkali in reactions of organic compounds. Decarboxylation and decarboxylation. A. N. Nomenzov, K. A. Pecherskaya, and G. Ya. Uretskaya. *Bull. acad. sci. U.R.S.S., Class. sci. chim.* 1948, 240-5.  $\text{C}_6\text{H}_5\text{CO}_2\text{H}$  (15 g.), 5 g. dry powd. KF, and 50 ml.  $\text{PhNO}_2$  were heated to  $130^\circ$ , when gas evolution and formation of  $\text{CHCl}_3$  took place; the distn. was continued until all volatile matter was removed, giving 70%  $\text{CHCl}_3$ . Heating 3 g.  $\text{p-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{CO}_2\text{H}$  and 1 g. KF to  $120^\circ$  for 0.5 hr., followed by distn. with 50 ml.  $\text{H}_2\text{O}$  and extra. with  $\text{Et}_2\text{O}$ , gave 0.8 g.  $\text{p-MeC}_6\text{H}_4\text{NO}_2$ , m.  $66^\circ$ .  $\text{PhC}_6\text{H}_4\text{CO}_2\text{H}$  (10 g.), passed in 20-30 min. over pieces of KF in a tube heated to  $325^\circ$  in a N atm., gave 6.2 g.  $\text{PhMe}$  (84%). Similarly, 15 g. anthranilic acid gave 7.2 g.  $\text{PhNH}_2$ . Heating 20 g. adipic acid and 10 g. KF 3 hrs. to  $250-300^\circ$  with distn. of the volatile matter, gave 65% cyclopentanone, b.p.  $125-30^\circ$ ; similarly 18 g. pimelic acid and 7 g. KF gave cyclohexanone, b.p.  $154-5^\circ$  (no yield given). Chloral (30 g.), 14 g. KF, and 50 ml. abs.  $\text{EtOH}$  heated with slow distn. (a spontaneous reaction occurs at the outset) gave 7 g.  $\text{HCO}_2\text{Et}$  and 21.5 g.  $\text{CHCl}_3$ .  $\text{C}_6\text{H}_5\text{CH}_2\text{CO}_2\text{H}$  (20 g.) and 12 g. KF heated to  $160^\circ$  gave 9 g. acrylic acid, b.  $139-41^\circ$ . Thus, F ion has well-expressed properties of a base in reactions with org. compds. Speculations about the mechanism are presented.

G. M. Kosolapoff

ASAC-5.4.4 DETAILED LITERATURE CLASSIFICATION

REG-5708137

10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100

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|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p><b>CA</b></p> <p><b>Organomercury compounds. XL. Synthesis of aromatic organomercury salts through arylazoacetic acids.</b> A. N. Nemeyanov and G. A. Reutov. <i>Izv. Akad. Nauk S.S.S.R., (Mol. Khim. Nauk 1966, 316-31); C.A. 42, 1671.</i> Salts of arylazoacetic acids with <math>HgCl_2</math> readily yield arylmercury chlorides. The character of the reaction is similar to that exhibited by the double diazonium mercury salts, i.e. the mechanism is homolytic: <math>PhN:NCO_2K</math> (Thiele, <i>Ber.</i> 28, 2001) (2 g.) was added in 0.5 hr. to 8.7 g. <math>HgCl_2</math> in 100 ml. <math>Me_2CO</math> at room temp. with stirring, which was continued 0.5 hr., after which the solvent was distd. and the residue was washed with NaCl and <math>H_2O</math>; extn. with <math>Me_2CO</math> gave 1.78 g. (64%) <math>PhHgCl</math>, m. 251-2°, and 1.03 g. <math>HgCl_2</math>; the use of <math>HgBr_2</math> gave 40% <math>PhHgBr</math>, m. 276°. <math>p</math>-<math>MeC_6H_4N:NCO_2K</math> (by hydrolysis of the amide with cold aq. alkali, filtration at 80°, cooling and washing the orange product with <math>H_2O</math>-<math>H_2O</math>) (2.03 g.) treated with 8.1 g. <math>HgCl_2</math> as above gave 1.09 g. (33%) <math>p</math>-<math>MeC_6H_4HgCl</math>, m. 236-7°, and 1.49 g. <math>HgCl_2</math>; the <math>p</math>-<math>NO_2</math> analog gave 42% <math>p</math>-<math>NO_2C_6H_4HgCl</math>, m. 265°, the <math>p</math>-<math>Br</math> analog gave 33% <math>p</math>-<math>BrC_6H_4HgCl</math>, m. 250°, and <math>HgCl_2</math>.</p> |  | <p><b>K p-sulfophenylazidoformate</b> (from 10 g. K salt of p-sulfophenylazidoformate in the min. amt. of hot water, treated with hot 4 g. <math>KNO_3</math> in 20 ml. <math>H_2O</math> and 20 ml. <math>H_2SO_4</math>, followed by filtration and cooling; yield 7 g. decomp. 255° after loss of water of crystn.) (10 g.) was hydrolyzed 1 hr. in the cold by 3.6 g. <math>KOH</math> and 30 ml. <math>H_2O</math>, warmed until clear, filtered, and cooled, yielding 6 g. of the K salt of p-sulfophenylazidoformic acid, yellow needles, decomp. about 265°, insol. in org. solvents, sol. in water; this (1.94 g.) added in 0.5 hr. to 3.4 g. <math>HgCl_2</math> in 100 ml. <math>Me_2CO</math> with stirring at room temp. in the presence of 0.7 g. powd. Cu, stirred 0.5 hr., the solvent removed, and the product extd. from the dry residue in the form of p-sulfophenylmercury II sulfate (31%) (see J. Gen. Chem. (U.S.S.R.) 4, 713 (1934) for properties). K-2-naphthylazidoformate (1.8 g. from the hydrolysis of fresh 2-CuH<sub>2</sub>N<sub>2</sub>CONH<sub>2</sub> by 60% excess aq. alkali at 80°) and 8.1 g. <math>HgCl_2</math> gave 41% 2-CuH<sub>2</sub>HgCl, m. 270-1°. <math>PhHgCl</math> (1 g.) in 25 ml. <math>Me_2CO</math> treated with 1.2 g. <math>PhN_2CO_2K</math> and refluxed 2 hrs. yielded 94% <math>PhHg</math> (from EtOH) and <math>HgCl_2</math> (94%).</p> |
| <p>418-114 RETROLOGICAL LITERATURE CLASSIFICATION</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |  |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |
| <p>10</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |  |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |

NESMEYANOV, A. N.

PA 7/49T13

USSR/Chemistry - Mercury Compounds May/June 48  
Chemistry - Synthesis

"Information From the Field of Mercury Organic  
Compounds," A. N. Nesmeyanov, O. A. Reutov,  
Chair of Org Chem, Chem Faculty, Moscow State U,  
5 pp

"Iz Ak Nauk SSSR, Otdel Khim. Nauk" No 3

Describes synthesis of aromatic mercury organic  
salts through aryl nitrocarboxylic salts. Submit-  
ted 20 Sep 1947.

7/49T13

NESMEIANOV, A. N

R. Kh. Freidlina, Alexandra Kochetkov and A. N. Nesmeianov, The Quasi complex  
Compounds of Thallium. P. 4455

SO: Bulletin of the U.S.S.R. Academy of Sciences (Chemistry Series)  
Izvestia Akad. Nauk, S.S.S.R., No. 4, 1948.

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |  |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|
| <p>1926 The Effect of Structural Factors on Conjugation Phenomena. I. The Mobility of Hydrogen Atoms in Cyclic Ketones of Various Structure. A. N. Nesmeyanov, D. N. Korsanov, K. A. Pecherskaya, and Z. N. Parnes. <i>Izvestiya Akad. Nauk S.S.S.R., Otd. Khim. Nauk</i>, No. 6, 582-7(1948)(in Russian).</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |  |
| <p>Heavy water was used for the substitution of D for H in the <math>\alpha</math> position in cyclic ketones. Such substitutions are correlated with the general mobility of the H atom in the sequence <math>\text{CH}-\text{CO}-</math> that must be regarded as a system of conjugated bonds <math>\text{H}-\text{C}-\text{C}=\text{O}</math>, analogous to the known <math>\text{C}-\text{C}-\text{C}=\text{O}</math>. Thus, in cyclohexanone all four <math>\alpha</math> hydrogens, and in 2,2,4-trimethylcyclohexanone the unique <math>\alpha</math> hydrogen, are replaced, whereas in the bicyclic camphenone the reaction is forbidden on account of the presence, in the <math>\alpha</math> position, of the foot of the <math>-\text{CH}_2-</math> bridge. In the procedure adopted the substance investigated was heated (for 50 to 70 hr and in the presence of <math>\text{K}_2\text{CO}_3</math>) with water containing a known quantity of <math>\text{D}_2\text{O}</math>. The reaction product, separated from water, was analyzed by charring, and the formed water was tested for D content by the specific gravity method. In this way the number of H atoms replaced was determined, and the result was checked by the D defect in water separated from the reaction product.</p> |  |
| <p>1926-1948 METALLURGICAL LITERATURE CLASSIFICATION</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |  |
| <p>1926-1948</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |  |

NESMEYANOV, An. N.

PA 64/49T2

Chemistry - Analytical      Jan/Aug 48  
Chemistry - Indicators, Radioactive

"Use of Radioactive Indicators in Analytical  
Chemistry," M. B. Neyman, Gor'kiy, An. N.  
Nesmeyanov, Moscow, 31 pp

"Uspekhi Khim" Vol XVII, No 4

Presents an extensive tabular description of re-  
sults obtained from use of radio-active elements  
for qualitative and quantitative determination  
of elements and substances, followed by a list of



"APPROVED FOR RELEASE: Monday, July 31, 2000

CIA-RDP86-00513R001136620

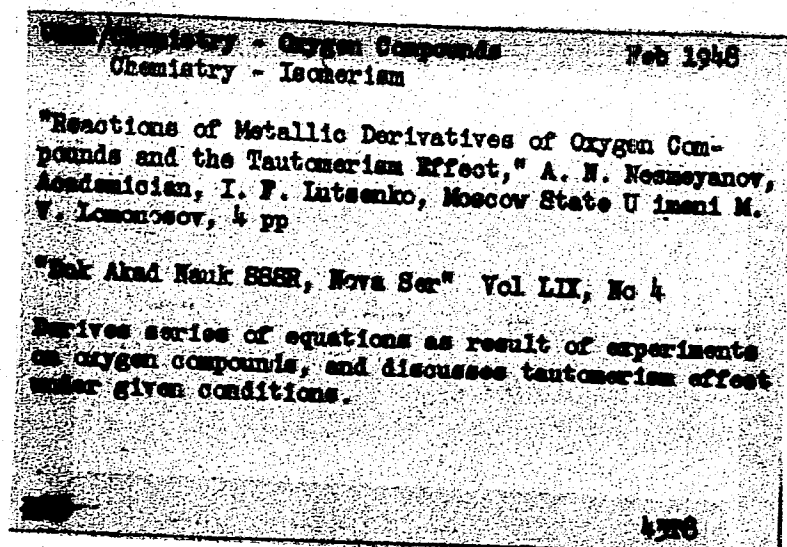
64/4912

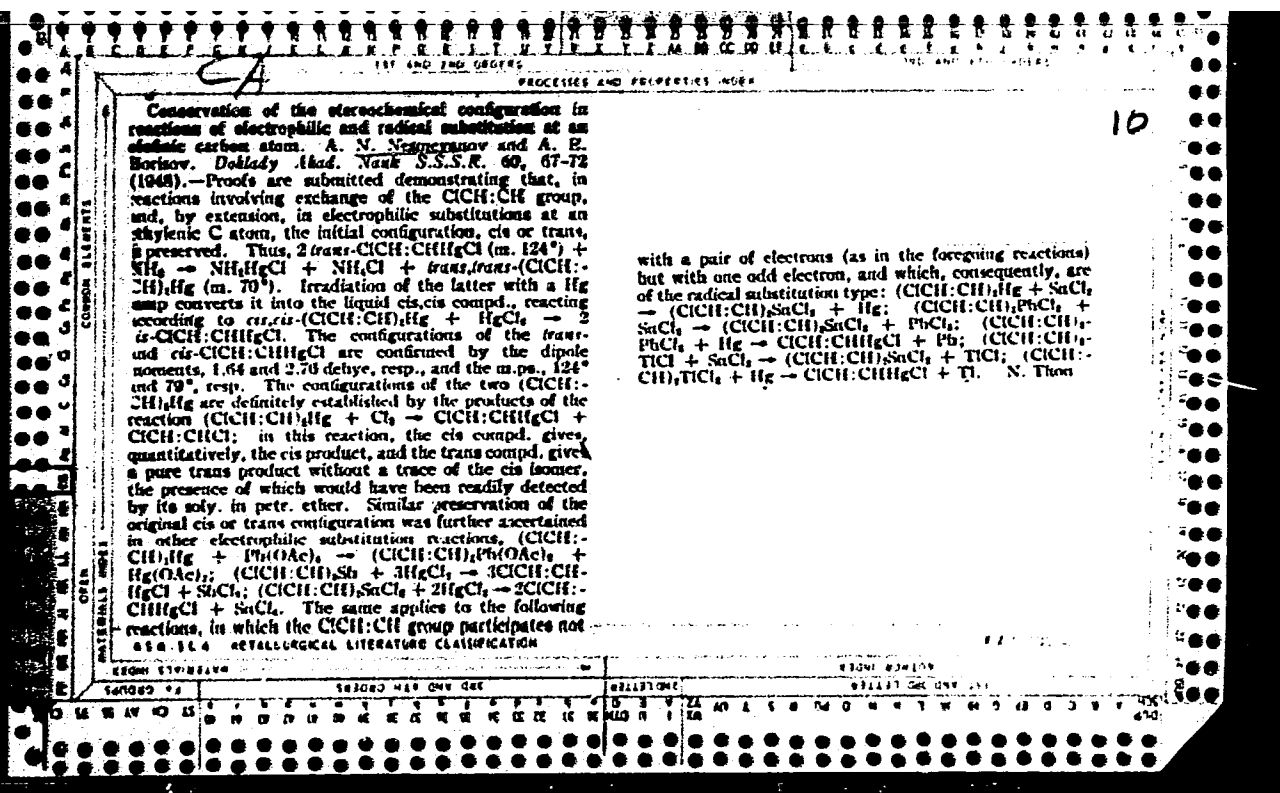
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NESMEYANOV, A. N.

PA 43/43TB





NESMEYANOV, A. N. Acad

PA 45/49T12

USSR/Chemistry - Magnesium Halide  
Chemistry - Ketones

Dec 48

"Structure and Reaction Capacity of the Magnesium  
Halide Enolates of Ketones," Acad A. N. Nesmeyanov,  
V. A. Sazonova, Ye. B. Landor, Moscow State U, imeni  
M. V. Lomonosov, 4 pp

"Dok Ak Nauk SSSR" Vol LXIII, No 4

Comprehensive study of bromomagnesium derivatives of  
beta, beta-diphenylpropionessitylene. Gives chemical  
properties of two bromomagnesium enolates of beta,  
beta-diphenylpropionessitylene and their reactions  
with benzoyl chloride. Submitted 6 Oct 48

45/49T12

NESMEYANOV, A., ACADEMICIAN

USSR

Chairman of the Committee of Stalin Prizes in Science and Invention (1949)

"New Victories of Soviet Science," Izvestia, 1949.

Current Digest of the Soviet Press, Vol. 1, No. 15, 1949, page 20. (In ~~the~~  
Library)

Quasicomplex compound of phenylethynyl methyl ketone  
with mercuric chloride. A. N. Kozmyanov and N. K.  
Kochetkov. *Izv. Akad. Nauk S.S.S.R., Khim. i  
Ned. 1949, 365-10.*—PhC<sub>2</sub>CCOMe (5 g.) and 100 ml.  
satd. HgCl<sub>2</sub> soln. in satd. NaCl shaken 4 hrs., with fur-  
ther addn. of 5 g. ketone, gave 97% adduct, 1-phenyl-1-  
chloro-2-(chloromercurio)-1-buten-3-one, m. 112-113° (from  
chloroform), easily decarboxyl. by hot aq. solvents. Treatment  
with 40% HCl gave a yellow oil, by 120-130° identified as  
1-phenyl-1-chloro-1-buten-3-one; (II); 2,4-dinitrophenyl-  
hydrates, m. 184-5°; osone, m. 94-5°. Treatment of  
the Hg deriv. with 5% KI soln. with shaking gave PhC<sub>2</sub>-  
CCOMe and a 91% yield of long. Hg in the aq. layer;  
satd. NaCl similarly gave 1, as did HgCl<sub>2</sub>, AcBr, and similar  
reagents. PhC<sub>2</sub>CCOMe (4.5 g.) in 20 ml. AcOH treated  
at 5° with 1.22 g. dry HCl in AcOH, let stand 2 hrs., and  
heated 1 hr. to 60° gave 2.7 g. I. G. M. Kosolapoff.

10

CA

Structure and reactivity of halomagnesium enolates of ketones. A. N. Nemeyanov, V. A. Sazonova, and E. H. Landor (M. V. Lomonosov State Univ., Moscow). *Doklady Akad. Nauk S.S.S.R.* 68, 395-8(1948); cf. C.A. 42, 6744a. — The metal derivs. of keto-enols have either one or the other structure; the concept of mesomeric ion is inadmissible. Addn. of 25 g. 2,4,6-Me<sub>3</sub>CrCl<sub>3</sub>·COCl<sub>2</sub>·Cl<sub>2</sub>Ph in Et<sub>2</sub>O to PhMgBr soln. (68 ml.; 0.27 g./ml.) and refluxing 3 hrs. gave 54% (β,β-diphenylpropyl)methylene bromomagnesium enolate, cryst. powder from CCl<sub>4</sub>-cyclohexane; with aq. NH<sub>4</sub>Cl it yields (β,β-diphenylpropyl)methylene, m. 82°. The latter with PhMgBr in Et<sub>2</sub>O gave 88% of the enolate which is a stereoisomer of the former deriv., as it is much less sol. in CCl<sub>4</sub>. The 2 enolates with BaCl<sub>2</sub> gave the stereoisomeric benzoates of the enols, m. 162° and 145°, resp. The MgBr enolate of either type treated with Me<sub>2</sub>Ni, followed by BaCl<sub>2</sub>, gave the benzoate, m. 145°. G. M. K.

CA

Quasimolecular compounds, hypocoordination, and tautomerism. A. N. Kuz'minov and V. A. Razonova. *Izv. Akad. Nauk S.S.S.R., Otdel Khim. Nauk* 1969, 422-34. —The arguments of Chertanov (cf. preceding abstr.) are criticized, with the contention that tautomerism by definition involves a reversible isomerization. In the present work it is shown that organometallic compounds of radicals contg. C—O (capable of enol-keto isomerization) do not display tautomerism and exist in the form of metal enolates, with metal-to-oxygen link, rather than in

the form of the currently accepted ionic structure with a mesomeric org. ion (except for the possible case of ammonium enolates). The support for the concept lies in monomers of rather stable "cis" and "trans" forms of the enolates in reactions of organometallic derivs. Addn. of 53 g.  $\text{PhCH:CHCOCl}$  to 52 g. mesitylene and 41.3 g.  $\text{AlCl}_3$ , followed by standing and 1.5-2 hrs. on a steam bath, gave 78% (benzylidenecetyl)mesitylene (I), m. 63°. b. 195°. Addn. of this (20 g.) in 50 ml.  $\text{Et}_2\text{O}$  to  $\text{PhMgBr}$  (from 12.56 g.  $\text{PhBr}$ ) in 40 ml.  $\text{Et}_2\text{O}$ , followed by 1.5 hr. on a steam bath and decompr. with aq.  $\text{NH}_4\text{Cl}$ , gave 61% (1,1-diphenylpropionyl)mesitylene (II), m. 125° (from abs.  $\text{EtOH}$ ). The prepn. of the subsequent  $\text{MgBr}$  deriv. of I was done in anhyd. conditions in a pure N atm. To 64 ml. filtered  $\text{PhMgBr}$  soln. (0.21 g./ml.) was added 100 ml. dry  $\text{Et}_2\text{O}$ , followed by 25 g. I in 20 ml.  $\text{Et}_2\text{O}$ , the mixt. heated 3 hrs., and the solvent evapor. until a ppt. formed; this on filtration and drying represented a 54% yield of II.  $\text{MgBr}$  enolate, which can be crystd. from  $\text{C}_6\text{H}_6$ -cyclohexane; it is a colorless solid, contg. 1  $\text{Et}_2\text{O}$  sol. in  $\text{C}_6\text{H}_6$ , insol. in  $\text{Et}_2\text{O}$ , and on decompr. with  $\text{NH}_4\text{Cl}$  yields 100% II. Addn. of 80 ml.  $\text{Et}_2\text{O}$  to 48 ml.  $\text{PhMgBr}$  soln. (same concn.), followed by 25 g. II in 70 ml.  $\text{Et}_2\text{O}$ , and heating 1.5 hrs., partially removing the solvent, and filtration, gave 88% of a cryst. II- $\text{MgBr}$  enolate, also contg. 1  $\text{Et}_2\text{O}$ , which can be crystd. from the same solvents as the 1st form, but which is 10 times less sol. in  $\text{C}_6\text{H}_6$ ; with  $\text{NH}_4\text{Cl}$  it also gives II. The 1st form (A) (5 g.) in  $\text{C}_6\text{H}_6$  on treatment with 1.4 g.  $\text{BaCl}_2$  and heating 2 hrs., gave on  $\text{NH}_4\text{Cl}$  treatment 56% II-enol benzoate, m.

162° (from  $\text{Me}_2\text{CO}$ ). Similar reaction of the 2nd form (B) gave 47% of a II-enol benzoate, m. 145° (from  $\text{Me}_2\text{CO}$ ), which gives a depressed mixed m.p. The 2 benzoates are not interconvertible upon heating, irradiation, or by the action of iodine. Passage of air, freed of  $\text{Cl}_2$ , through 1.6 g. A in 20 ml. dry refluxing  $\text{Et}_2\text{O}$  for 2 hrs., followed by  $\text{NH}_4\text{Cl}$  treatment, gave after 5 crystals, 0.2 g. (α-bromo-1,1-diphenylpropionyl)mesitylene, m. 172° (from dry  $\text{EtOH}$ ), identical with the product of bromination of I in  $\text{CHCl}_3$ . Repetition of the above with 3.35 g. A, 20 ml.  $\text{Et}_2\text{O}$ , and  $\text{MgBr}_2 \cdot \text{Et}_2\text{O}$  (from 0.45 g.  $\text{Mg}$ ) added, gave 74% of the same product. Passage of air through B (with or without added  $\text{MgBr}_2$ ) failed to yield a  $\text{Br}$  deriv. of II; the usual decompr. of the mixt. only gave pure II. Boiling 4.6 g. A with 4 g.  $\text{Me}_2\text{NI}$  in  $\text{C}_6\text{H}_6$  4 hrs., followed by 1.2 g.  $\text{BaCl}_2$  and heating 2 hrs., gave upon decompr. by  $\text{NH}_4\text{Cl}$  soln. 1.2 g. (31%) II-enolate benzoate, m. 145°, identical with that obtained previously from B; in addn. 0.4 g. unidentified matter, m. 127°, was isolated from the filtrate. Similar reaction of B gave 37% of the same benzoate. Irradiation of a  $\text{C}_6\text{H}_6$  soln. of A with a Hg lamp 24 hrs., followed by warming 2 hrs. with  $\text{BaCl}_2$ , gave 30% II, and no benzoate of II-enol was found; similar treatment of B gave 20.7% II-enol benzoate, m. 145°. Addn. of 3 g. I in 15 ml.  $\text{Et}_2\text{O}$  to 11.5 ml.  $\text{Et}_2\text{O}$  soln. of  $\text{PhLi}$  (0.089 g.  $\text{PhLi}/\text{ml.}$ ), refluxing 45 min., and decompr. with  $\text{H}_2\text{O}$  gave 90% II. If before treatment with  $\text{H}_2\text{O}$  the soln. is warmed with  $\text{BaCl}_2$  0.5 hr., there is obtained 87% II-enol benzoate, m. 162°, but if  $\text{BaCl}_2$  is added to the reaction mixt. only after it has been freed of  $\text{Et}_2\text{O}$  and kept 2 hrs. at 100°, there is formed 30% of the isomeric benzoate, m. 145°, and a noncrystg. oil. Similar reaction with  $\text{MeOCH}_2\text{Cl}$  in  $\text{Et}_2\text{O}$  (0.5 hr. refluxing after the addn.) gave 40% solid C-MeO methylation product, m. 155°, as well as 20% oil, b. 216-16°, which does not crystallize and on hydrolysis yields  $\text{CH}_3\text{CO}$  and II; hence the latter product is an O-MeO methylation product of II. Addn. of 3 g. I and 20 ml.  $\text{Et}_2\text{O}$  to 13.8 ml.  $\text{PhLi}$  soln. in  $\text{Et}_2\text{O}$



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(0.0774 g./ml.) and refluxing 0.5 hr., followed by addn. of 40 ml.  $\text{C}_6\text{H}_6$ , distn. of the  $\text{Et}_2\text{O}$  in vacuo, refluxing the soln. either alone or with  $\text{Me}_2\text{Ni}$  30 min., and treatment with  $\text{BaCl}_2$  gave the II-enolate benzoate, m. 161-2°. If  $\text{Me}_2\text{Ni}$  was absent, while the presence of  $\text{Me}_2\text{Ni}$  led to formation of both benzoates in 7:2 ratio (mostly m. 145°). Addn. of 2 g. I and 40 ml.  $\text{Et}_2\text{O}$  to 6 ml.  $\text{PhLi}$  soln. (0.0864 g. in 1 ml.  $\text{Et}_2\text{O}$ ) and refluxing 0.75 hr., followed by 20 mins. reflux with 0.85 g.  $\text{BaCl}_2$  gave 70% II-enol benzoate, m. 145°, while the mother liquor gave a small amt. of

the isomer, m. 162°; similar reaction of I with  $\text{PhLi}$  in  $\text{Et}_2\text{O}$ , followed by treatment with  $\text{MeOCF}_3\text{Cl}$ , gave 38% *O*-MeO methylated product, m. 155°, and the petr. ether- $\text{Et}_2\text{O}$  mother liquor yielded 36% *O*-MeO methylated II, m. 92-3° (from  $\text{MeOEt}$ ), which on hydrolysis with concd.  $\text{HCl}$  gave II. Hence, the "double" action of  $\text{MgBr}$  and  $\text{Li}$  enolates is not a result of tautomerism nor does it establish an ionic nature of the org. residue in the enols.

G. M. Kinney

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Несмеянов, А. Н.,

Несмеянов, А. Н., Батуев, М. И. and Борисов, А. Е.  
Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1949, 567-9

CA: 44-2374/b

Raman spectra of chlorovinyl derivatives of mercury and antimony.

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CH NESMEYANOV, A. N.

Synthesis of stereoisomeric organotin compounds with ethylenic structure from organomercury cis-trans isomers and their rearrangement in ultraviolet light. A. N. Nesmeyanov, A. B. Borovoy, and A. N. Abramova (Inst. Org. Chem., Moscow). *Izv. Akad. Nauk S.S.S.R., Khim. Nauk* 1949, 550. Heating 10 g. *trans*- $\text{CICH}_2\text{CH=CHHgCl}$  and 25 g.  $\text{Na-Sn}$  (15% Na) in 30 ml.  $\text{C}_6\text{H}_6$  at 45-50° 3 hrs. in a H. atm. gave 40% *trans*-( $\text{CICH}_2\text{CH=CH}$ ) $_2\text{SnCl}_2$ , m. 120-1° (from petr. ether). Similarly the *cis*-Hg deriv. gave 38% of the *cis* isomer, b. 110.5°, n<sub>D</sub><sup>20</sup> 1.5821, d<sub>4</sub><sup>20</sup> 1.8688. Heating the *trans*-isomer with HgCl<sub>2</sub>

in EtOH yields  $\text{C}_6\text{H}_5$  and 77% *trans*- $\text{CICH}_2\text{CH=CHHgCl}$ , similarly, the *cis*-isomer yields the *cis*-Hg deriv. Irradiation of the molten *trans*-Sn deriv. with ultraviolet light 25 hrs. gave 40% *cis*-isomer. Heating 15 g. *trans*-( $\text{CICH}_2\text{CH=CH}$ ) $_2\text{Hg}$  with 2.75 g. pulverized Sn in EtOH slightly acidified with HCl to 20° 1.5 hrs. gave 90% Hg and 20% *trans*-( $\text{CICH}_2\text{CH=CH}$ ) $_2\text{SnCl}_2$ , m. 120-1°, and 1.5% *cis*-( $\text{CICH}_2\text{CH=CH}$ ) $_2\text{SnCl}_2$ , b. 81.5°, n<sub>D</sub><sup>20</sup> 1.5802, d<sub>4</sub><sup>20</sup> 2.0062. Similarly *cis*- $\text{CICH}_2\text{CH=CHHgCl}$  gave 78% Hg, and an incompletely sepl. mixt. of *cis*- $\text{R}_2\text{SnCl}_2$  and  $\text{R}_2\text{SnCl}_2$ , b. 55.7°, n<sub>D</sub><sup>20</sup> 1.5714, and b. 87-90°, n<sub>D</sub><sup>20</sup> 1.5826, resp. *trans*- $\text{R}_2\text{SnCl}_2$ , m. 76-8°, and the  $\text{R}_2\text{SnCl}_2$  deriv. were obtained in 2-30% yields, along with the  $\text{R}_2\text{SnCl}_2$  from  $\text{R}_2\text{Hg}$  and Sn and were isolated by fractional crystn. Addn. of pyridine to *trans*- $\text{R}_2\text{SnCl}_2$  in EtO gave a complex, ( $\text{CICH}_2\text{CH=CH}$ ) $_2\text{SnCl}_2 \cdot 2 \text{C}_5\text{H}_5\text{N}$ , very difficultly sol. in org. solvents.

G. M. Kozlov

Transformation of *trans*-2-chlorovinyl metallorganic compounds of mercury and tin into the *cis*-isomers under the influence of peroxides. A. N. Seleznev, A. E. Ruzikov, and V. D. Vilychevskaya (Inst. Org. Chem., Moscow). *Izv. Akad. Nauk S.S.S.R., Khim. Nauk* 1949, 378-81. Heating *trans*- $\text{ClCH}=\text{CHHgCl}$  for 2-24 hrs. to 100-105° in xylene,  $\text{MePh}$ , dioxane, or  $\text{CCl}_4$  with traces of  $\text{Ac}_2\text{O}$ ,  $\text{H}_2\text{O}_2$ , or  $\text{Na}_2\text{O}_2$  converts the *trans* into the *cis*-isomer in 22-100% yields. Hydroquinone stops the isomerization. A similar reaction of *trans*- $\text{ClCH}=\text{CHSnCl}_2$  in xylene with  $\text{H}_2\text{O}_2$  in hrs. at 105° gave 80% of the *cis*-isomer. Probably the reaction proceeds by a chain mechanism. G. M. K.

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11:2 chlorovinyl)thallium chloride. A. N. Nemyayev, A. R. Borzov, and R. I. Shepeleva (Inst. Org. Chem., Moscow). *Izv. Akad. Nauk. S.S.S.R., (Div. Chem. Nauk)* 1949, 3828. —  $\text{TiCl}_4$  (2.13 g.) and  $\text{cis-(Cl-CH:CH)}_2\text{Hg}$  (0.45 g.) in 16 ml.  $\text{Et}_2\text{O}$  gave on standing 10 hrs. 22.1%,  $\text{cis-(ClCH:CH)}_2\text{HgCl}$ , m. 145.6° (from  $\text{Et}_2\text{O}$ ). This in 1 g. and 0.2 g.  $\text{NaCl}$  in abs.  $\text{EtOH}$  after standing 4 hrs. gave 18.5%,  $\text{TiCl}_4$ , and 38%,  $\text{cis-(ClCH:CH)}_2\text{HgCl}$ , m. 149.3°, mp 136.6°. Staking 0.1 g.  $\text{cis-R}_2\text{HgCl}$  with 0.1 g.  $\text{Hg}$  in  $\text{MeOH}$  90 hrs. gave 100%,  $\text{TiCl}_4$  and 0.00 g.  $\text{cis-(ClCH:CH)}_2\text{Hg}$ . Similarly,  $\text{TiCl}_4$  and  $\text{cis-trans}$  (some mixt. of  $\text{R}_2\text{Hg}$  in  $\text{Et}_2\text{O}$ ) gave 10%,  $\text{trans-(ClCH:CH)}_2\text{HgCl}$ , m. 166.7° (from dil.  $\text{EtOH}$ ), and 13%,  $\text{cis-isomer}$  which seps. more slowly from the soln.; only  $\text{cis-R}_2\text{HgCl}$  was isolated from the residue. Ultraviolet irradiation of  $\text{trans-(ClCH:CH)}_2\text{Hg}$  35 hrs., followed by standing for 7 days gave 48%,  $\text{cis-(ClCH:CH)}_2\text{HgCl}$ , m. 72° (from ligroin); in addn. some  $\text{cis-trans-R}_2\text{Hg}$  is formed, extd. by letting the  $\text{Et}_2\text{O}$  soln. of the mixt. stand with  $\text{TiCl}_4$  15 min. and weighing the  $\text{trans-R}_2\text{HgCl}$  formed; the yields of the  $\text{cis-trans-Hg}$  deriv. range from 0 to 24.9%.  
G. M. Kosolapoff

Organomercury compounds. XLIV. Properties of mercury halomercaptides and conjugation of simple bonds. A. N. Nesmeyanov and N. K. Kochetkov (Moscow State Univ.). *Izv. Akad. Nauk S.S.S.R., Otdel Khim. Nauk* 1949, 887-91; cf. C.A. 43, 7413d. —  $(\text{Cl}_2\text{C})_2\text{Hg}$  (0.25 g.) (I) with 0.45 g.  $\text{Ph}_3\text{P}$  in 20 ml.  $\text{C}_6\text{H}_6$  in a N atm. showed no tendency to react in 12 hrs.; an  $\text{EtOH}$  soln.

gave the same result. The *Et* analog of I is similarly inactive, even on a steam bath, with  $\text{Ph}_3\text{P}$ . Treating  $(\text{BrC}_6\text{H}_4)_2\text{Hg}$  with 20% KCN in a N stream for 1 hr. led to hydrolysis, which evolved  $\text{BrC}_6\text{H}_4\text{CN}$ , detected by passing through alk. Hg cyanide soln., which regenerated  $(\text{BrC}_6\text{H}_4)_2\text{Hg}$ ; the residual soln. with  $\text{H}_2\text{S}$  gave 92%  $\text{HgS}$ ; a similar result was obtained with 10%  $\text{HCl}$  at room temp., while 20% aq. KI did not react at room temp. but readily gave  $\text{BrC}_6\text{H}_4\text{I}$ , detected as above, on warming 2 hrs. on a steam bath (53% of the Hg recovered as the sulfide).  $(\text{BrC}_6\text{H}_4)_2\text{Hg}$  (5 g.) with  $\text{PhMgBr}$  (from 4.5 g.  $\text{PhBr}$ ) in a N stream yielded Hg bromomercaptide, as shown by carbonation to  $\text{BrC}_6\text{H}_4\text{COOH}$ , m. 84-5° (0.5 g.); 1.1 g.  $\text{Ph}_3\text{Hg}$  was also recovered, as well as 0.3 g.  $\text{PhHgBr}$  and 2.2 g. unreacted Hg deriv.  $(\text{PhC}_6\text{H}_4)_2\text{Hg}$  (4 g.) with  $\text{PhMgBr}$  (from 2.2 g.  $\text{PhBr}$ ) on refluxing 3 hrs. gave after carbonation 1.03 g.  $\text{Ph}_3\text{Hg}$  and 1.06 g.  $\text{PhC}_6\text{H}_4\text{COOH}$ , m. 120°. Hence the Hg halomercaptides do not possess quasicomplex properties of  $(\text{CH}_3\text{C}_6\text{H}_4)_2\text{Hg}$  deriv. since they are unable to form a new multiple bond between the C atoms, while the chlorovinyl deriv. are able to do so.

XLV. Preparation of monohalomercury ketones and aldehydes from enol acetates and their reactions, with C- and O-alkylation and oxylation. A. N. Nesmeyanov, I. F. Lutsenko, and Z. M. Turanova. *Ibid.* 1949, 601-4. — Addn. of 4.3 g.  $\text{CH}_3\text{CHOAc}$  with shaking to 16 g. Hg acetate in 75  $\text{H}_2\text{O}$ , followed by addn. of 3.3 g. KCl (after filtration of Hg salts), gave 100% (chloromercuri)acet-aldehyde,  $\text{ClHgCH}_2\text{CHO}$ , decomp. 129-31°. Similarly  $\text{CH}_3\text{CH}_2\text{CHOAc}$  gave 71.5%  $\text{ClHgCH}_2\text{CH}_2\text{CHO}$ , m. 108-4° (stable to  $\text{KMnO}_4$  at room temp.). Cyclohexenyl acetate gave 80% 2-(chloromercuri)cyclohexanone (I), m. 134-5° (from  $\text{H}_2\text{O}$ ), while cyclohexenyl acetate gave 71% 2-(chloromercuri)cyclopentanone, m. 149-50° (from  $\text{Me}_2\text{CO}$ ). Addn. of 7.5 g.  $\text{AcCl}$  to 25 g.  $\text{ClHgCH}_2\text{CHO}$  in xylene gave, after 1 hr. 48%  $\text{CH}_3\text{CHOAc}$  and a residue which by its soly. in cold  $\text{HCl}$  with a little quinoline added after 1 hr. to remove unreacted  $\text{AcCl}$  gave 66%  $\text{MeC}(\text{CH}_3)_2\text{OAc}$ , while I. similarly gave 57% cyclohexanone enol acetate. Likewise reactions with  $\text{BrCl}$ , which required 6-8 hrs. heating to 50° for completion, gave, resp.: 66%  $\text{CH}_3\text{CHOBr}$ , b. 72-3°,  $n_D^{20}$  1.5279,  $d_4^{20}$  1.047; 63%  $\text{CH}_3\text{CH}_2\text{CHOBr}$ , b. 67°,  $n_D^{20}$  1.5171,  $d_4^{20}$  1.047; 63% cyclohexanone enol bromate, b. 146-7°,  $n_D^{20}$  1.5368,  $d_4^{20}$  1.0765.  $\text{ClHgCH}_2\text{CHO}$  (25 g.) and 25 g.  $\text{Ph}_3\text{CCl}$  in  $\text{C}_6\text{H}_6$  let stand overnight and refluxed 2 hrs. gave 65%  $\text{Ph}_3\text{CCH}_2\text{CHO}$ , m. 99-101° (from  $\text{MeOH}$ ). Similarly  $\text{ClHgCH}_2\text{CH}_2\text{CHO}$  gave 40%  $\text{Ph}_3\text{CCH}_2\text{CH}_2\text{CHO}$ , m. 140-1° (from  $\text{H}_2\text{O}$ ), while  $\text{ClHgCH}_2\text{CH}_2\text{CH}_2\text{CHO}$  gave 36%  $\text{Ph}_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{CHO}$ , m. 164° (from  $\text{H}_2\text{O}$ ). XLVI. Addition of mercuric chloride to acetylenic acids and esters. A. N. Nesmeyanov, N. K. Kochetkov, and V. M.

*Dehydrois.* *Ibid.* 1940, 77-82.— $\text{HgCl}_2$  with acetylenic acids gives adducts which behave like quaternary complex compounds. Addition of 1 g.  $\text{HC}(\text{CO}_2\text{H})$  to 10 ml. satd. aq.  $\text{HgCl}_2$  in satd.  $\text{NaCl}$  gave in 3 hrs. 91%  $\text{CICH}:\text{C}(\text{HgCl})\text{CO}_2\text{H}$ , m. 178-8° (decomps.; from  $\text{H}_2\text{O}$ ), sol. in  $\text{EtOH}$ , but  $\text{H}_2\text{O}$ , poorly sol. in  $\text{CHCl}_3$  and  $\text{C}_6\text{H}_6$ . Similarly tetrolic acid gave 64%  $\text{MeCCl}:\text{C}(\text{HgCl})\text{CO}_2\text{H}$ , m. 12° (from  $\text{MeOH}$ ), while  $\text{HC}(\text{CO}_2\text{Me})$  gave 86%  $\text{CICH}:\text{C}(\text{HgCl})\text{CO}_2\text{Me}$ , m. 161-3° (from aq.  $\text{MeOH}$ ), and Et tetrolate gave in 12 hrs. 85%  $\text{MeCCl}:\text{C}(\text{HgCl})\text{CO}_2\text{Et}$ , m. 84.0-4.5° (from  $\text{C}_6\text{H}_6$ , petr. ether). Likewise,  $\text{PhC}(\text{CO}_2\text{Me})$  gave in 2 weeks 74%  $\text{PhCIC}:\text{C}(\text{HgCl})\text{CO}_2\text{Me}$  (I), m. 122-3° (from  $\text{MeOH}$ ), while  $(\text{CCO}_2\text{Me})$  gave in 3 days 73%  $\text{MeCCl}:\text{C}(\text{HgCl})\text{CO}_2\text{Me}$  (II), m. 145.0-5.5° (from  $\text{MeOH}$ ). I (35 g.) shaken 4 hrs. with 125 ml. 40%  $\text{HBr}$  gave 11% *trans*-8-chlorooctanoic acid, m. 142°, as well as some  $\text{PhC}(\text{CO}_2\text{Me})$ . Likewise, 35 g. II after 15 min. gave 78% *di*-Me chlorofumarate, bp 113-14°, converted to the free acid, m. 191°, by heating 10 hrs. with 5%  $\text{HBr}$ . Treatment of  $\text{CICH}:\text{C}(\text{HgCl})\text{CO}_2\text{H}$  with 5%  $\text{KI}$  1 hr. gave 93% of  $\text{Hg}$  in aq. soln. and yielded  $\text{ICH}:\text{C}(\text{CO}_2\text{H})$ ; similarly,  $\text{MeCCl}:\text{C}(\text{HgCl})\text{CO}_2\text{H}$  in 8 hrs. gave 91.3%  $\text{Hg}$  in soln. and yielded tetrolic acid, while  $\text{CICH}:\text{C}(\text{HgCl})\text{CO}_2\text{Me}$  in 3 days gave 80.5%  $\text{Hg}$  in soln. and yielded  $\text{CH}_2:\text{C}(\text{HgCl})\text{CO}_2\text{Me}$ , and  $\text{MeCCl}:\text{C}(\text{HgCl})\text{CO}_2\text{Et}$  gave in 18 hrs. 89.5%  $\text{Hg}$  in soln. and yielded phenylmethylenephosphonic

lone, while I gave in 3 days 70.25%  $\text{Hg}$  in soln. and yielded  $\text{PhC}(\text{CO}_2\text{H})$ ; in similar reactions with satd.  $\text{NaCl}$  were obtained, resp., 86%  $\text{Hg}$  in soln. in 2 days, 96%  $\text{Hg}$  in soln. in 36 hrs., from the 1st 2 substances, while the rest failed to react appreciably. II in 3 weeks with 5% aq.  $\text{KI}$  gave di-Me iodofumarate, m. 59.5-1.5° (from lig. rotn), and some  $(\text{CCO}_2\text{Me})$ , while 25%  $\text{KI}$  in  $\text{Me}_2\text{CO}$  gave instantaneously 16.9% of the iodofumarate and 93%  $\text{NaCl}$ .  
G. M. Kosolapoff

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Influence of the structural factors on conjugation phenomena. I. Mobility of hydrogen atoms in various cyclic ketones. A. N. Nesmeyanov, D. N. Kursanov, K. A. Pecherskaya, and Z. N. Parnes (Inst. Org. Chem., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk* 1949, 592-7. — 2,2,6-Trimethylcyclohexanone completely exchanges one H for a D atom after 70 hrs. at 130° in enriched H<sub>2</sub>O; cyclohexanone exchanges 4 H atoms for D atoms in 50 hrs. at 100°. Spiro[4.5]decan-6-one exchanges between 1 and 2 H atoms for D in 70 hrs. at 130°. No exchange takes place with camphenone or camphorquinone; this is explained by nonexistence of conjugation between the C=O group and C-H, which follows from Hückel's rule. II. Mobility of hydrogen atoms in acetylacetone and its cobalt and aluminum salts. A. N. Nesmeyanov, D. N. Kursanov, T. A. Smolina, and Z. N. Parnes. *Ibid.* 598-600. — CH<sub>3</sub>Ac, kept 70 hrs. at 17° in H<sub>2</sub>O enriched with D<sub>2</sub>O in the presence of dioxane showed exchange of 2 H (within 15%) for 2 D. The Co salt and the Al salt show no enrichment by D. The result is explained on the basis of impossibility of conjugation of the residual C-H bond with C=O due to perpendicularity of the axes of the C-H link and that of the  $\pi$ -function of the C=O group, as well as to Favourski's rule (C.A. 45, 2449), which forbids allene formation in 6-member rings. G. M. K.



CA

Introduction of the trichloromethyl group into an aromatic nucleus by decarboxylation of trichloroacetic acid in the presence of aromatic hydrocarbons. A. N. Nekremyayev, K. A. Pecherskaya, and G. Ya. Uretskaya (Inst. Org. Chem., Moscow). *Izv. Akad. Nauk S.S.S.R., Otdel Khim. Nauk* 1949, 607-10. — The liberation of the  $\text{CCl}_3$  anion during the decarboxylation of  $\text{Cl}_3\text{CCOOH}$  (I) (cf. C.A. 42, 4924g) permits its utilization for trichloromethylation of aromatic hydrocarbons. Presence of the  $\text{CCl}_3$  group is shown by its hydrolysis to  $\text{CO}_2\text{H}$ . Heating 10 g. I, 12 g.  $\text{CuCl}_2$ , and 2 drops pyridine 1 hr. to 155-75°, followed by treating with hot 2 N NaOH for 0.5 hr. gave 4% 1- $\text{CCl}_3\text{C}_6\text{H}_5$ , m. 150-0.5°. Addn. of a few drops of pyridine to a molten mixt. of 25 g. I, 30 g.  $\text{CuCl}_2$ , and 2 g. dry  $\text{CuCl}_2$  and heating 1 hr. at 155-70° gave 23% 1- $\text{CCl}_3\text{C}_6\text{H}_5$  and 4 g. of a mixt. of  $\text{CHCl}_3$  with  $\text{Cl}_3\text{CCOCl}$  (identified as the anilide, m. 94°); when  $\text{Cu}$

trichloroacetate was used as catalyst the yield of 1- $\text{CCl}_3\text{C}_6\text{H}_5$  rose to 35%. Similarly 10 g. I, 15 g. fluorene, 0.8 g.  $\text{CuCl}_2$ , and a little pyridine at 150-85° gave 14% 6-fluorene-carboxylic acid, m. 240°. Anthracene (10 g. I, 25 ml.  $\text{PhNH}_2$ , (without solvent much decompos. occurs), 10 g. I, and a little pyridine similarly gave 6% 6-anthracene-carboxylic acid, m. 205-7° (decompos.). Phenanthrene similarly gave (a solvent is unnecessary) 9% mixed isomeric phenanthrene-carboxylic acids, m. 181-91°. Tech. xylene gave an unstated amt. of isomeric  $\text{Me}_2\text{CCl}_2\text{C}_6\text{H}_4$ , m. 85-105°. G. M. Kozlovskii

CH

Decomposition of arylidiazonium salts. A. N. Nesmeyanov and O. A. Reutov (Inst. Org. Chem., Moscow). *Izv. Akad. Nauk S.S.S.R., (Dokl. Khim. Nauk 1949, 611-22).*—The mechanism of the decompn. of arylidiazonium salts is discussed from the point of view of formation of radicals.  $\text{PhN}_2\text{CONH}_2$  (30 g.) and 30 g.  $\text{H}_2\text{O}$  treated with 45 ml. 1:1 KOH with stirring (continued 30-40 min.), then with 30 ml.  $\text{H}_2\text{O}$ , heated on a steam bath, and filtered hot gave 30 g.  $\text{PhN}_2\text{CO}_2\text{K}$  (I), which must be used immediately after drying by suction. Addn. of 29.5 g. I to 32.7 g.  $\text{trans-ClCH:CHHgCl}$  in 200 ml. dry  $\text{Me}_2\text{CO}$  gave  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{C}_6\text{H}_6$ , as well as some  $\text{C}_6\text{H}_5$ .

18.5%  $\text{PhHgCl}$ , a trace of  $\text{Ph}_2\text{Hg}$ , and 12.5%  $\text{trans-PhCH:CHCl}$ . Similarly I with  $\text{CH}_3\text{CH}_2\text{CHO}$  gave  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{Hg}$ ,  $\text{PhHgCl}$ ,  $\text{C}_6\text{H}_6$ , and  $\text{AcH}$ . I (100 g.) and 150 g.  $\text{AcH}$  gave a resinous mass contg. a 1,4-diketone; reduction of the mass with  $\text{Zn-Hg-HCl}$  and bromination of the product gave  $\text{Ph(CHBr)}_2\text{Ph}$ , m. 180°. Similar reaction of I with  $\text{Ph}_2\text{CO}$  gave 10.5%  $\text{PhC}_6\text{H}_4\text{Br}$ , m. 103°. I with a large excess of  $\text{EtO}_2\text{CCl}$  in  $\text{Me}_2\text{CO}$  gave 54%  $\text{C}_6\text{H}_5$ , 17.5%  $\text{PhNHCO}_2\text{Et}$ ,  $\text{BrOEt}$ ,  $(\text{EtO})_2\text{CO}$ , and 13%  $\text{CO(NHPh)}_2$ , m. 236°. I and  $\text{AcCl}$  gave  $\text{C}_6\text{H}_5$ ,  $\text{Ac}_2\text{O}$ , and  $(\text{CH}_3\text{COCl})_2$ . Clemmensen reduction of the tar formed from  $\text{AcPh}$  and I, along with the  $(\text{BrCl})_2$ , gave some  $p\text{-(H}_2\text{N)}_2\text{C}_6\text{H}_4$ , and  $\text{PhNMe}_2$  (identified as  $\text{AcNHPh}$ ). G. M. Kozlov

CA

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1,6-Addition of mesitylmagnesium bromide to dimethylvinylcarbinol acetate. A. N. Nemeyanov, R. Kh. Freidlina, and A. K. Kochetkov (Inst. Org. Chem., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk* 1949, 623-30. —  $CH_2:CHCMe_2OAc$  (I), b. 121-2.5°,  $n_D^{20}$  1.4118,  $d_4^{20}$  0.8639, was obtained in 45% yield by heating 70 g. carbinol, 70 g. dry  $AcONa$ , and 100 g.  $Ac_2O$  15 hrs. to 90-100°; a by-product, 3-methyl-2-butene acetate, b. 151-2°,  $n_D^{20}$  1.4283,  $d_4^{20}$  0.9240, also forms. Hydrogenation of I over  $Pd-CaCO_3$  gave  $AcOCMe_2Et$ , b. 123-4°,  $d_4^{20}$  0.8770,  $n_D^{20}$  1.4020. I (40 g.) and 2,4,6- $Me_3C_6H_3MgBr$  (from 100 g.  $Me_3C_6H_3Br$ ) in  $Et_2O$  gave after refluxing 30 hrs. 37.5% mesitylene and 19.5 g.  $C_{11}H_{14}$ , b. 143-4.5°,  $n_D^{20}$  1.5190,  $d_4^{20}$  0.9042, identified as 1-mesityl-3-methyl-2-butene, which with H over Pt in  $AcOH$  gives the *sald. deriv.*, b. 134-5°, while bromination in  $CCl_4$  gives the dibromide, m. 68-9°.

G. M. Kosolapoff

CA

*Organic Chemistry*

Metalloorganic compounds of lithium, sodium, potassium, rubidium, and cesium. K. A. Kochetkov and T. V. Tikhonova. *State. Medits. Zhurnal. Sverdlovsk. Inst. Org. Khim., Akad. Nauk S.S.S.R.* 1949, No. 1, 378 pp. Mercury organic compounds. L. G. Makarova and A. N. Neumaynov. *Ibid.* 1945, No. 3, 146 pp. Metallo-organic compounds of elements of the third group. K. A. Kochetkov and A. N. Neumaynov. *Ibid.* 1945, No. 4, 124 pp. Metalloorganic compounds of elements of the fourth group. K. A. Kochetkov. *Ibid.* 1947, No. 8, 131 pp. Aromatic organic compounds. R. Kh. Prokhorova. *Ibid.* 1945, No. 7, 140 pp. —Compilations contain the methods of synthesis, properties, reactions, and analysis of these compounds. M. Houch

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"Quasi-Complex Compounds, Hyperconjugation and Tautomerism," A. N. Nesmeyanov, V. A. Sazonova, Moscow State U imeni M. V. Lomonosov, Chair of Org Chem, 162 pp

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 4

pp. 412-38

Shows that bromomagnesium and lithium derivatives of oxo compounds, e.g., B,B diphenylpropionals, tylenes, have the fixed structure of enolates because it is natural for them to appear as cis- and trans-isomers. Refutes previous opinion on their

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tendency for reversible isomerization (tautomerism) and the mesomeric ion in their ionic structure. Explains dual reactivity of such compounds (to give C- and O- alkylated or acylated oxo and enol derivatives) by the union of O-, M-, and C-C- bonds. Submitted 22 Apr 49.

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